PRINCIPLES OF IGNITION

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A DESCRIPTION OF THE MAIN FACTS AND THEORIES RELATING TO THE IGNITION OF INFLAMMABLE GAS MIXTURES BY SPARKS, FLAMES, INCANDESCENT SOLIDS, AND OTHER SOURCES

BY

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PREFACE

THERE are two classes of engineers who have a practical interest in the subject of ignition—those concerned with internal combustion engines, and those concerned with the prevention of explosions in mines and factories, and it is for such engineers that this book is primarily intended. The purpose of the book is to describe simply and briefly the principal facts relating to the ignition of inflammable gas mixtures by sparks, flames, incandescent solid particles, and other localized sources. A description is also given of certain theories which have been put forward to co-ordinate or explain the actions of such sources.

Since the well-known pioneer work of Prof. W. M. Thornton a great deal of systematic experimenting has been done in this field of investigation, and at present the main results of this work lie scattered in scientific periodicals. The time seems appropriate for bringing together in a compact form what in my opinion appear to be the more important results. In the preparation of the book I have not only included the main results of my own work but also drawn freely on the contents of the large collection of papers by others which I have gathered during the past twenty years, and I am grateful to the Editors of the *Philosophical Magazine* for permission to make full use of certain papers published in that journal. For the sake of simplicity and clearness of exposition I have avoided crowding the book with a description of unimportant details. Also I have neglected much of the earlier pioneer work which now has only historic interest. A list of references at the end of the book gives particulars of the publications of which I have made use, but this list must not be regarded as a bibliography of the subject.

The subject of ignition by localized sources, like so many other scientific subjects, can be divided into two parts—experimental and theoretical. In Chapters I to VI, I have confined myself strictly to an account of facts ascertained by

PRINCIPLES OF IGNITION

CHAPTER I

SPARKS AND SPARK MEASUREMENTS

In the study of the ignition of inflammable gas mixtures by electric sparks, it is convenient to recognize three types of sparks. These may be termed respectively, capacity, inductance, and fusion sparks. A capacity spark (sometimes referred to as a jump, condenser, condensed, or high tension spark) is obtained when a charged condenser is discharged across a gap between metal or other electrodes spaced at a fixed distance apart. An inductance spark (sometimes termed a break, or low tension, spark) is obtained by separating a pair of contacts or breaking a conductor in an inductive circuit carrying a current. Fusion sparks are obtained when, for example, rough metal bodies forming parts of a live electric circuit (inductive or non-inductive) are rubbed together. A spectacular shower of fusion sparks can be produced by rubbing across the surface of a file or other rough metal body connected to one pole of an electric battery, the free end of a thin wire attached to the other pole.

For some purposes the word "spark" is used in a restricted sense to denote only the spark obtained by applying a sufficiently high voltage to the electrodes of a fixed gap, the term "arc" being used to designate the spark obtained on separating a pair of contacts in an inductive circuit. But in the study of gaseous ignition by means of sparks it is more convenient to use the term spark in the wider sense, and to distinguish between the different kinds of sparks by the qualifying words above mentioned.

Capacity Sparks

A spark of this kind is usually very bright in appearance, and of very short duration. When examined by a spectroscope

the spectrum is found to correspond mainly with that of the air or other gas in which the spark occurs. When examined by a rotary mirror the spark is found to present the appearance of a single line or dot, similar to that seen by direct vision, or a succession of separate lines or dots. The voltage required to produce a capacity spark depends on what is termed the "sparking voltage" of the gap in which the spark is produced, and varies with the width of the gap, the shape of the gap electrodes, and the pressure and character of the gas in the gap. The current flowing in such a spark may be very high, though the quantity of electricity conveyed may be small. The energy required to produce a capacity spark is expressed by the quantity $\frac{1}{2}CV^2$, where C is the capacity of the condenser and V the sparking voltage of the gap. The amount of energy actually dissipated in the spark may, however, be considerably less than is represented by this quantity, especially when a condenser having a solid dielectric is used in the spark circuit. In experimental work having for its object to ascertain the least energy required to ignite a given gas by a capacity spark it is advisable to use air-condensers.

Inductance Sparks

A spark of this kind is usually less bright in appearance than a capacity spark. When viewed through a spectroscope, the spectrum is found to correspond mainly with that of the vapour of the material of the contacts between which the spark occurs. Its duration may vary greatly, and in some instances the duration may be very long in comparison with that of a capacity spark. When examined in a rotary mirror an inductance spark presents the appearance of a band or ribbon of flame. The current in the spark is always less than that in the circuit prior to separation of the contacts, but the total quantity of electricity transferred may be large. The energy required to produce an inductance spark is expressed by the quantity $\frac{1}{2}Li^2$, where L is the inductance of the circuit and i the current flowing prior to separation of the contacts. The total energy actually dissipated in the spark may, however, be considerably less than that amount owing to extinction of the spark before the available electromagnetic energy has been

expended. On the other hand, the energy dissipated may exceed that amount if the voltage across the electrodes is sufficient to maintain the spark, and it is necessary to keep this fact in mind when measuring the energy required to ignite a given gas by an inductance spark, as it will be found that the energy as measured by the quantity $\frac{1}{2}Li^2$ diminishes with increase of the impressed voltage.

Fusion Sparks

These consist of small fused and incandescent particles derived from the contacting substances through which the current is passing. When the object of the study of such sparks is to minimize explosion or fire risks, it is necessary to recognize that gaseous ignitions can be effected by fusion sparks. They may be as potent igniting agents as the sparks produced by the pyrophoric appliances commonly used for igniting cigarettes, or the gas issuing from the burners of domestic heating and cooking apparatus. But they may also be harmless, as it is possible to produce an impressive display of fusion sparks in an inflammable gas mixture without causing ignition. The systematic study of these sparks is difficult, as they do not lend themselves to quantitative experiments. But some very interesting work has been done by R. S. Silver and S. Paterson on ignition by single solid particles shot through inflammable gas mixtures, yielding valuable information from which may be inferred the main conditions affecting ignition by fusion sparks, and this is described in Chapter IV.

Brush Discharge

Another kind of electric discharge, which is not a spark in the ordinary sense of the term, but which must be mentioned because it is capable of causing ignition, is the brush discharge, or corona, formed on, for example, a pointed or thin conductor carrying a high voltage. The brush discharge is not a very potent igniting agent. At one time it was believed that a brush discharge could not ignite an inflammable gas mixture, but this has been disproved. Where a fire or explosion risk exists, the brush discharge must be regarded as a possible

cause of ignition. The work by R. W. Sloane described in Chapter II is valuable in this connection.

High Tension Magneto or Induction Coil Sparks

For ignition of the explosive charges in an internal combustion engine use has been made of pure capacity sparks, and also of pure inductance sparks. The spark most extensively used is of the kind produced by a magneto, or an induction coil (now usually referred to as an ignition coil). Because of its peculiar character it is necessary to describe its main features in detail. The essential parts of the apparatus used to provide such a spark are shown diagrammatically in Fig. 1. Here *a* is

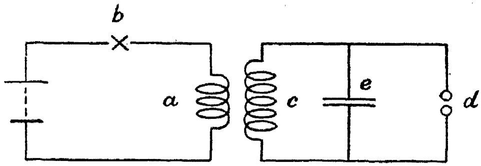

FIG. 1

the primary winding in which current is generated, or to which current is supplied, this winding being mounted on an iron core, and *b* is the interrupter by which the circuit containing the winding *a* is intermittently made and broken. The winding *c* is the secondary winding and this is connected to the spark gap *d*. The winding *c* is arranged coaxially, or is otherwise magnetically linked, with the primary winding. When a current flows in *a* there is generated a magnetic flux which interlinks both *a* and *c*. On interrupting the current in *a* the magnetic flux disappears, and in so doing generates a voltage at the electrodes of the gap *d*. If the voltage is sufficiently high it produces at *d* a spark which is usually of a composite character, consisting of both capacity and inductance components, these being due to the capacity and inductance of the apparatus. The inductance is associated with the windings *a*, *c*, and the capacity is distributed over the winding *c*, the parts associated with the gap electrodes, and the conductors connecting the electrodes to the winding *c*. To complete the diagram the capacity is shown by the conventional representation of a

condenser and is indicated by *e*. This capacity receives a charge during the short time interval which elapses between the interruption of the current in *a* and the occurrence of the spark at *d*. When the spark passes the first effect results from the discharge of *e*. But this discharge does not usually exhaust the energy of the magnetic field established by the current in *a*, and the residue, or some of it, serves to maintain the discharge at the gap until the voltage falls to a value at which the discharge cannot be continued. The first part of the discharge is called the capacity component of the spark, and the second part the inductance component. The two components can usually be distinguished quite easily on inspection of the spark. This will be seen to consist of a bright core (capacity component) surrounded by a flame (inductance component). When the spark is examined with the aid of a rotary mirror, the image seen in the mirror has an appearance such as is represented by Fig. 2. At the commencement of the image is seen the bright line *a* corresponding to the capacity component, and following it is seen the less bright and flame-like band or ribbon *b* corresponding to the inductance component. Usually the latter presents a striated appearance as indicated by the transverse lines in the part *b*, the significance of these lines being that the inductance component is of a pulsating or oscillatory character. This latter feature is, however, of no interest in the study of ignition phenomena, and it is sufficient to know that the spark produced by an ignition coil or magneto is of composite character consisting of the two components mentioned. A further feature that will be noticed in the image seen in the rotary mirror is a blue line *c* along one side of the inductance component. This is the cathode glow and indicates that the discharge (at least during the duration of the inductance component) is unidirectional.

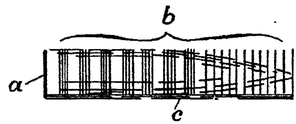

FIG. 2

The energy rendered available for spark production when a current i flows in a (Fig. 1) is $\frac{1}{2}Li^2$, where L is the inductance of the primary winding. When this energy is released by the interruption of the current in a its first effect is to charge the

distributed capacity of the system (represented by the condenser e) to the voltage corresponding to the sparking voltage. The energy then stored in the secondary side of the system is $\frac{1}{2}CV^2$, where C is the capacity of the system and V the sparking voltage of the gap d. This amount of energy (less losses) appears in the capacity component of the spark, and the residue, that is to say the difference between $\frac{1}{2}Li^2$ and $\frac{1}{2}CV^2$ (less losses), appears in the inductance component.

It will be apparent that the capacity component must always be present. If the energy due to the current in the primary winding is not sufficient to charge the capacity to the sparking voltage of the gap a spark cannot occur. When a spark does occur it must possess at least the capacity component, and the residual energy, if any, will appear in the succeeding inductance component. The amount of energy discharged in the capacity component is a fixed quantity so long as the sparking voltage of the gap and the capacity associated with the spark-producing apparatus remain constant. Variation of either of these factors, as by varying the gap setting, by lengthening or shortening the cables connecting the secondary winding to the gap, or by enclosing the cables in an earthed metal tube, will affect the quantity $\frac{1}{2}CV^2$. Otherwise the energy discharged in the capacity component is constant. The energy discharged in the inductance component may vary greatly, and seeing that it depends on the difference between $\frac{1}{2}Li^2$ and $\frac{1}{2}CV^2$, it can be affected (assuming C to be constant) by variations in the primary current in excess of that required to produce the capacity component, the width of the spark gap, and the insulation leakage associated with the spark gap or other parts of the system.

When a variable condenser is placed in the position e (Fig. 1) and the capacity of the condenser is varied while the spark is being examined in a rotating mirror, the effect on the distribution of energy in the two components of the spark can readily be seen. With a given width of gap, increase of capacity causes increase of the capacity component and diminution of the inductance component. Sufficient increase will cause the inductance component to disappear. Further increase will cause the spark to disappear suddenly, as the energy available

will then be insufficient to charge the condenser to the sparking voltage. Likewise, keeping the capacity constant, alteration of the width of the gap will vary the distribution of energy in the two components of the spark. Moreover, alteration of the current in the primary winding, keeping the capacity constant, will cause the inductance component to vary. Further, by appropriate adjustment of the primary current, the capacity, or the gap width, the discharge may then produce a multiple spark, that is to say a spark consisting of a succession of sparks each consisting of only a capacity component, or a capacity component followed by a short inductance component. The breaking up of the discharge from an ignition coil into a multiple spark can be effected by a blast of air blown across the gap while the spark is passing. Oscillograph records show that multiple sparks sometimes occur in engines, a condition which may be attributable at least in part to the violent turbulence of the gases sweeping over the sparking plug electrodes. Whether the fact that a discharge may sometimes occur in the form of a multiple spark is of any practical consequence in the ignition of the gas in an internal combustion engine, especially one operating on a petrol or like mixture, is a matter on which a good deal of controversy has centred, and it is doubtful whether any definite conclusion has yet been reached, but in the writer's opinion the fact is of no practical importance, as ignition ought to (and usually does) result from the first part of the discharge. The significant fact to be recognised is that a magneto or induction coil spark may have and usually has the two components above described, and as will be shown later the important one of the two is the capacity component.

The above brief account of the various kinds of sparks of interest in the study of ignition problems is probably sufficient for the reader's immediate purpose. For fuller information relating to ignition coil sparks the writings of E. Taylor-Jones[1, 2] and W. McFarlane[3] cited in the references at the end of this book are recommended.

Spark Measurements

Before a systematic study of spark ignition effects can be

apparatus with current from, say, a direct current service main operating at, say, 100 or 200 volts, but it would then be found that the spark energy as determined by the quantities L and i required to ignite a given gas would be less than when, for example, a 10-volt battery is used as the source of supply. This difference is attributable to the fact that while the spark is in existence, the current flowing in it is due not only to the dissipation of the energy represented by the quantity $\frac{1}{2}Li^2$, but also to additional energy supplied to the spark from the source and not contained in that quantity. It is necessary, therefore, to make the contribution supplied by the source during the sparking interval as low as possible, and this condition is satisfied by using a low voltage source. Some figures bearing on this point are given on page 17.

Production and Measurement of Capacity Sparks

A typical form of apparatus used in ignition experiments with capacity sparks is shown in Fig. 4. In this apparatus *a* is an adjustable spark gap in an explosion chamber *b*. Across the spark gap is connected a variable condenser *c* and this is charged through a diode thermionic valve *d* from an induction coil *e*. By suitably adjusting the primary current of the coil and the rate of operation of its interrupter, the condenser can be charged at any desired rate, this latter being adjusted to cause successive sparks to occur at the gap at any convenient frequency, such as one per second. Preferably one side of the gap and the associated parts of the apparatus are earthed as shown in the diagram.

The energy required to produce each spark is represented by the quantity $\frac{1}{2}CV^2$ where C is the electrostatic capacity of the condenser and V the sparking voltage of the gap. The principal precaution to be observed is that of using an air condenser. This is perhaps unfortunate because it necessitates a condenser of bulky and clumsy form. But when a condenser having a liquid or solid insulator between the plates is used, extraordinary irregularities can be obtained in the measurements of the energy required to produce ignition sparks. This is no doubt due to the residual charge remaining in the condenser after the occurrence of the spark, which charge may not only be

large but it may also vary greatly. When the dielectric between the condenser plates is air the residual charge (if any) is both small and regular, so that $\frac{1}{2}CV^2$ can be taken as a fair measure of the energy dissipated in the spark. Another precaution to be observed is that the capacity of the apparatus other than

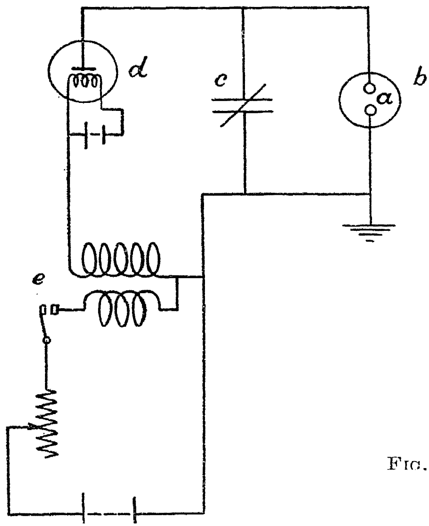

FIG. 4

that associated with the condenser should be as small as possible, and the part of the apparatus lying between the condenser and the spark gap should be as non-inductive as possible.

It might be considered appropriate to mention at this stage another factor upon which the capacity-spark energy required to ignite a given gas depends, namely, the width of the gap and the shape of the gap electrodes, but this factor is dealt with in Chapter II.

In using the above-described methods of measuring inductance and capacity sparks, it must always be kept in mind that what is measured is the energy required to produce the spark, and the assumption involved is that, having adopted suitable precautions in the design of the ignition apparatus, a large and

regular proportion of this energy will be dissipated in the spark. It is very difficult, however, to ensure that apparently identical pieces of apparatus used by different experimenters are in fact identical, and consequently the results obtained by different experimenters following the same routine on similar gas mixtures may not be exactly the same, a condition which it is necessary to remember when comparing the results of different experimenters.

It will be apparent that measurements useful in the systematic study of the ignition of gas mixtures cannot easily be made on the complex sparks given by magnetos or ignition coils. As regards the capacity component, the sparking voltage can readily be determined, but not the capacity associated with the spark generator, the gap, and their connections. The energy supplied to or developed in the primary winding of the spark generator can also be measured, but this is no guide to the amount of energy apportioned to the two parts of the spark. For the systematic study of ignition by sparks it is, therefore, advantageous to use simple sparks derived from the discharge of a condenser, or the discharge of an inductive winding.

CHAPTER II

INCENDIVITY OF ELECTRIC SPARKS AND CORONA DISCHARGES

By incendivity is meant that property of an igniting agent (such as a spark, flame, or hot solid) whereby it is able to cause ignition. The term was introduced by the writer in the early stages of his work on ignition by sparks, to avoid any undesirable theoretical implication that might be associated with such terms as intensity, power, activity, strength, which were then in common use. The term ignitability might have been adopted, but this was rejected on account of possible confusion with the word inflammability, which denotes a characteristic property of the medium ignited.

A fact which is soon encountered in a systematic study of spark ignition is that the amount of energy required to produce the least igniting spark (i.e. the spark just capable of igniting a particular gas mixture at a particular pressure and temperature) is not a constant, but varies with the character of the spark, the electrodes between which the spark is formed, and the apparatus used for producing the spark. This fact is (or was) probably more responsible than any other for raising doubts as to whether ignition by an electric spark can be regarded as a thermal action, and giving support to the alternative belief that the action of the spark is electrical.

Reflection on the results obtained in experiments with different sparks, however, soon suggests that the differences found ought never to have caused surprise, and that on the contrary, the mystery would have been more profound if they had been otherwise. It is necessary always to keep in mind the localized and transient character of the spark, and that its energy is expended in part usefully in performing its igniting function and in part uselessly in the regions of the gas mixture beyond that in which ignition is originated. It is to be expected, therefore, that the incendivity of a spark will to some extent depend on the rate at which its energy is dissipated. Further,

it is to be expected that the size and proximity of the spark electrodes will affect the incendivity of the spark. Moreover, it is necessary to remember that (as explained in the previous chapter) the spark energy is measured not in terms of the energy of the spark itself but of that required to produce the spark, and this latter may not only be a larger quantity but its amount will depend in part on the character of the apparatus used for providing the spark.

Experiments with Capacity Sparks

Reverting to Fig. 4, it will be apparent that the condenser is the probable seat of the principal energy losses in the apparatus. The losses in the wires connecting the condenser and gap electrodes can be made negligibly small. But the condenser can give rise to misleading results when the dielectric is solid or liquid. Using condensers with glass, ebonite, solid and liquid paraffin as the dielectric, the writer obtained most irregular results. A high degree of precision and consistency was difficult if not impossible to secure, and the energy required to produce a spark that could ignite a given gas was greater than when air condensers were used. With an air condenser, that is to say, a condenser made from metal plates separated by air, the energy losses attributable to the condenser were found to be negligibly small, and not only were consistent results obtained, but also a very high standard of accuracy. With this apparatus, therefore, variations of incendivity can be regarded as due entirely to conditions associated with the spark and the gap. Here there are several variable factors to be considered. They are the material of the gap electrodes, the shapes and areas of the electrode surfaces presented to the gap, and the width of the gap between the electrodes.

Experiments with various materials, namely platinum, nickel, zinc, aluminium, lead, and brass, showed that changes in the materials had no appreciable effect on the energy required to ignite a given gas mixture. This is not surprising when it is remembered that the spectrum of a capacity spark is chiefly that of the gas through which the spark passes. But variations of gap width and of electrode size and shape had large effects on incendivity. The results of two experiments will be quoted

in support of this statement.(4) These are recorded in the graph shown in Fig. 5. In this graph the ordinates represent joules, these values being calculated from the expression $\frac{1}{2}CV^2$, where V is the sparking voltage of the gap and C the capacity of the air condenser connected to the gap. Two curves are shown, these being marked A and B, and in the figure there are also shown the shapes of the gap electrodes used in obtaining

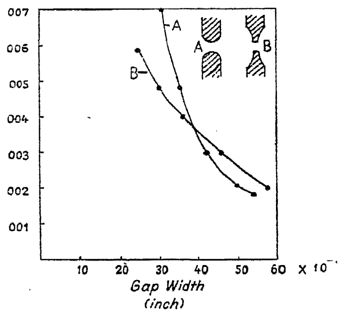

FIG. 5

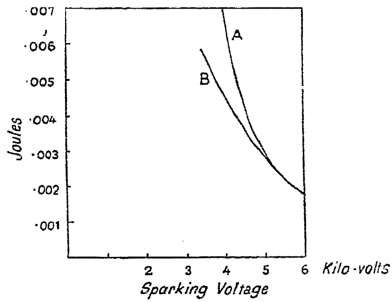

FIG. 6

the results represented by the curves. In one set of experiments the sparks were produced between a pair of electrodes shaped as shown by A. In the other a pair of electrodes shaped as shown by B were used. The electrodes were made from brass rods of $\frac{3}{16}$ in. diameter. Electrodes A had hemispherical ends. Electrodes B differed in that their ends were reduced to a diameter of about $\frac{3}{64}$ in. It will be noticed that in both curves the energy required to produce the least igniting spark falls rapidly with increase of gap width. Also it will be noticed that the energy required is affected greatly by the configuration of the electrode surfaces immediately adjacent to the gap. As the relationship between sparking voltage and gap width was not the same for the two pairs of electrodes, this relationship was ascertained, and the results shown in Fig. 5 are repeated in Fig. 6, in which the abscissae are expressed in kilo-volts. Fig. 6 also brings out the fact that the effect of electrode configuration vanishes when the gap is sufficiently wide. The gas used in the experiments recorded by the above-mentioned graphs was a mixture of 8·8 per cent methane in

air at atmospheric pressure and temperature. Essentially similar results were obtained with coal gas and blast-furnace

Experiments with Inductance Sparks

Looking again at Fig. 3, it will be apparent that here also are present several variable factors which may affect both the energy required to produce the least igniting spark and the incendivity of the spark. In this case the energy is measured by the quantity $\frac{1}{2}Li^2$ where L is the inductance of the winding b and i the current flowing in the system prior to interruption by the contact device d. The factors that require investigation are (1) conditions associated with the winding b, (2) the voltage applied to the system by the battery a or other energy source, and (3) conditions associated with the sparking electrodes d.

As regards conditions associated with the winding b,[(5)] six cylindrical coils were made all of the same length and having the same number of turns in each layer, but differing in the number of layers. The smallest coil had two layers, and the largest fourteen. The others had respectively four, six, eight, and ten layers. All coils were made from copper wire of the same size. Three sets of experiments were carried out. In the first the coils had no core, that is to say they were air-core coils with no metal associated with them other than the wire from which they were wound. In the next the coils were individually placed on a straight laminated iron core made from iron strips. In the third the coils were individually placed on one side of a rectangular laminated iron frame made from iron strips. In each experiment the inductance of the winding was measured and the current required to produce the least igniting spark was ascertained. The gas ignited was a mixture of Birmingham coal gas and air at atmospheric temperature and pressure. In each of the three sets of experiments the quantity $\frac{1}{2}Li^2$ was the same for all coils, but differed with the character of the core. No useful purpose would be served by quoting the results obtained with all the coils and it will be sufficient to quote those obtained with the fourteen-layer coils. These are given in the accompanying table.

No. of Layers in Winding	Core	Inductance (henry)	Current (amp.)	Energy ($\frac{1}{2}Li^2$ joule)
14	Air	0·01	0·35	0·0006
,,	Straight iron bar	0·07	0·17	0·0008
,,	Rectangular iron frame	0·56	0·09	0·0023

The results given in the table show that the energy required to produce the least igniting spark varied with the character of the core of the winding and was least with the air core. From this it is to be inferred that the larger amounts of energy required when the windings were mounted on iron cores were attributable mainly, if not wholly, to losses in the cores.

It has already been mentioned (page 10) that the energy required to produce the least igniting spark varies with the voltage impressed on the spark system. In this connection, the results of some experiments with an 8·8 per cent methane-air mixture will be quoted.(6)

Impressed Voltage 4 (Storage Battery)

Inductance of Winding (henry)		Current (amp.)	Energy ($\frac{1}{2}Li^2$ joule)
(1)	0·0214	0·77	0·00635
(2)	0·012	1·025	0·00630

Impressed Voltage 220 (D.C. Service Mains)

Inductance (henry)		Current (amp.)	Energy ($\frac{1}{2}Li^2$ joule)
(1)	0·0214	0·35	0·00130
(2)	0·012	0·4	0·00096

It will be noticed that the energy required to effect ignition and expressed as $\frac{1}{2}Li^2$ was greater with the low-voltage source than with the high-voltage source. This is attributable to the fact that when an inductance spark is established the current flowing in the spark is due in part to the dissipation of the

energy stored in the apparatus prior to occurrence of the spark and in part to the continued supply of energy from the source. When the impressed voltage is sufficiently low the second factor is negligibly small, but when high may be large. It is reasonable to assume that the actual energy required to ignite the gas was the same or substantially the same in all the experiments, but owing to the fact that the unmeasured portion attributable to the high-voltage source in the second set of experiments was appreciable the measured portion associated with the inductance was correspondingly less.

Another fact brought out by the experiments is that when a low-voltage source was used, the results were independent of variations of the inductance. But when the high-voltage source was used, the measured energy associated with the larger inductance was greater than that associated with the smaller inductance, and here a warning is required. In some measurements made by Prof. R. V. Wheeler[6] an opposite result was found. For example, he found the following, using an 8·5 per cent methane-air mixture.

IMPRESSED VOLTS 90

Inductance (henry)	Current (amp.)	Energy ($\frac{1}{2}Li^2$ joule)
0·031	0·42	0·0027
0·095	0·19	0·0017

These measurements serve well to bring out the limitations of the method of measuring spark energy used in the experiments, and to show how misleading the measurements might be when considered apart from the apparatus used in the experiments—a fact which is ever present in the minds of those who have worked on the subject, but not always recognized by those who have occasion to use the results and have not fully understood how much the results depend on the apparatus with which they were obtained.

Passing now to conditions associated with the electrodes of the contact device, it has already been mentioned that the spectrum of an inductance spark is mainly characteristic of

the metals of the electrodes between which the spark occurs, and it is reasonable to expect that the energy required to produce the least igniting spark depends to some extent on the metal of the electrodes. R. V. Wheeler[7] has investigated this aspect of the subject and obtained results which are given in the accompanying table.

Metal	Boiling Point (° C.)	Igniting Current for 8·35 per cent Methane-air Mixture
Cadmium	778	0·23
Zinc	918	0·25
Aluminium	1800	0·30
Silver	1955	0·32
Gold	2530	0·34
Copper	2310	0·38
Nickel	2330	0·39
Iron	2450	0·42
Platinum	2450	0·48

Other factors associated with the electrodes but which are not easily reducible to quantitative form and which affect the energy required to produce the least igniting spark are the surface areas of the electrodes and the rate of separation. In general a very slow or a very rapid rate of separation is attended by an increase in the energy required for ignition. There appears to be a particular rate of separation at which the energy required is least. Also the greater the area of the metal surfaces exposed to the spark and gas the greater is the spark energy required for ignition, the spark energy being measured as above described.

One other question in connection with inductance sparks which can be conveniently dealt with at this point is as to whether the incendivity of a spark produced by an alternating current is different from that of a spark produced by a direct current. In some of his earlier work, Professor W. M. Thornton[8] obtained evidence which led him to the conclusion that the incendivity of sparks produced in circuits carrying alternating currents was much less than that of sparks produced in similar circuits carrying direct current. In his words, "At all voltages much larger currents are required to produce ignition than with direct current." Consequently, "in places where electricity is used in the possible presence of inflammable

mixtures, as, for example, in coal mines, alternating currents are much safer than continuous, where open sparking may occur, and the higher the frequency the greater the safety." The first of these two conclusions excited a good deal of interest and raised an important practical question in the minds of those concerned with safety in mines. There is no obvious reason why sparks in a.c. circuits should be essentially different from sparks in d.c. circuits. As the matter was regarded as an important one, experiments were made by H. F. Coward and R. V. Wheeler,[9] and they failed to find any difference between the incendivities of a.c. and d.c. sparks in similar circuits. Using an 8·5 per cent methane-air mixture the results they obtained were as follows—

Circuit Voltage	Periodicity/sec.	Inductance (henry)	Igniting Current (amp.)
d.c. 35	—	0·098	0·24
a.c. 35·3 (crest value)	50	0·098	0·24 (crest value)

At about the same time and independently, the writer also made some experiments.[6] Using an 8·5 methane-air mixture, he found that in a given circuit a direct current of 0·415 amp. was required to cause ignition. It will be noticed that this current value is considerably larger than Coward and Wheeler's, but this is of no consequence, as the least igniting current required in an inductive circuit to ignite a given gas mixture varies with the inductance. Keeping other circuit conditions the same, the current was changed from d.c. to a.c. with the following results—

Periodicity/sec.	Igniting Current (amp.) (crest value)
68	0·410
200	0·420

It will be seen, therefore, that the conclusions reached by Thornton were not confirmed. The evidence of the other experiments cited shows that there is no difference between

the incendivities of a.c. and d.c. sparks produced under otherwise similar conditions.

Relative Incendivities of Capacity and Inductance Sparks

As a general statement it can be said that a capacity spark dissipating a given quantity of energy is more effective in igniting a particular gas mixture than an inductance spark dissipating the same quantity of energy. But to avoid possible misunderstanding it is necessary to explain this statement, as it is easy to find figures that appear to be in disagreement with it. For example, in Fig. 5 it was shown that with the electrodes *A* placed at a short distance apart the energy required

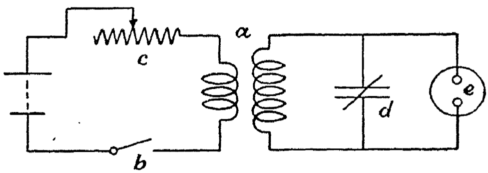

FIG. 7

to ignite an 8·8 per cent methane-air mixture was 0·007 joule, and on page 17 it was stated that the amount required in a low voltage inductive system for the same gas mixture was 0·00635 joule. But it was also shown in Fig. 5 that with the same electrodes spaced farther apart the energy required for ignition fell to 0·002 joule. The statement that a capacity spark is more effective than an inductance spark is true only if the sparks of the two kinds are comparable in size, and are produced between comparable electrodes. In some experiments by the writer, in which a coal gas-air mixture was used and in which the sparks were fairly comparable, the energy required to produce the least igniting capacity spark was 0·00025 joule and that for the least igniting inductance spark was 0·0006 joule. It must be conceded, however, that by comparison of figures obtained under different experimental conditions the statement that in general the incendivity of a capacity spark is greater than that of an inductance spark may appear to rest on an insecure foundation. But a simple experiment with the apparatus illustrated by Fig. 7 places the statement beyond

dispute. In this figure, *a* indicates a small induction coil, *b* an interrupter and *c* a variable resistance in the primary circuit, *d* a variable air condenser across the secondary circuit, and *e* a spark gap in an explosion chamber. The electrodes of the gap, whilst not sharply pointed, presented only very small areas at their ends to the spark path between them. The experiment was carried out on a weak coal gas-air mixture (at atmospheric pressure and temperature), requiring considerably more energy for its ignition than a mixture of maximum inflammability. With the condenser adjusted to its minimum capacity, the current in the primary winding of the coil was adjusted to such a value that the spark obtainable with that current was incapable of igniting the gas. The spark was of the composite character described in Chapter I, having both capacity and inductance components, and the inductance component was easily detectable by the eye. Obviously some preliminary trials were necessary to find the right conditions, but having found them the results were that with the condenser adjusted to its minimum capacity the spark failed to cause ignition, but on increasing the capacity sufficiently, ignition resulted, the only change made in the adjustment of the apparatus being that of the condenser. The energy required to produce the sparks was in each case $\frac{1}{2}Li^2$, where L is the inductance of the primary winding of the coil and i the current passed through that winding. The total energy in the spark was not varied by adjusting the condenser, but the distribution of energy between the two components was varied, increase of capacity causing more of the energy to be concentrated in the capacity component at the expense of the inductance component. In this experiment the two components of the spark were fairly comparable, as both were of the same length and occupied the same region of the gap. Moreover, there was very little lateral spreading of the inductance component in the gap. The chief difference between the two components was their duration, the capacity component having a very short duration relatively to the inductance component. Consequently, the experiment can be regarded as a fair test of the effect on incendivity of variation of the rate at which the energy is dissipated in the spark. The fact established by this

experiment is that incendivity is increased by increasing the rate of energy dissipation, and it follows that the incendivity of a capacity spark is greater than that of a comparable inductance spark dissipating the same amount of energy.

In conjunction with the above-described experiment must be considered another and important experiment by Professor E. Taylor-Jones.[10] His spark gap electrodes were 8 mm. diameter with spherical ends set 0·15 mm. apart. The sparks were produced by a magneto. He found that with no condenser in the secondary circuit a current in the primary circuit of 0·7 amp. sufficed to give a spark that would ignite the gas he was using. But with a condenser in that circuit the spark failed to effect ignition even when the current was increased to 10 amp., giving a spark of nearly 200 times as much energy. On examining the sparks photographically he found that the spark obtained with the condenser in action was concentrated in the narrowest part of the gap between the electrodes, but without the condenser the spark beginning at the narrowest part of the gap spread outwards towards the sides and in spreading lengthened. In this experiment the different sparks were not comparable. With the condenser in action the sparks were pure capacity sparks of very short length and diameter. Without the condenser the capacity component was also short and of small diameter, but the inductance component was of larger diameter and of greater mean length due to spreading between the convex surfaces of the electrodes. For the present purpose the significance of this experiment is that the incendivity of a capacity spark can be much less than that of an inductance spark of greater length and diameter dissipating the same amount of energy.

On this question of the relative incendivities of the two components of a magneto or induction coil spark the following experiment is also interesting. The apparatus used was the same as that shown in Fig. 7, but with the condenser removed. The gas mixture was a weak coal gas and air mixture such that easily measurable differences of gap width and primary current were sufficient to cause the difference between non-ignition and ignition. By trials with different mixtures, primary currents, and gap widths, a "border-line" condition

was found in which either a small increase of primary current or a small increase of gap width would change a non-igniting spark into an igniting spark. Moreover, electrodes presenting only small end faces to the gap were chosen, and the width of gap used was such that a small difference in gap width would (apart from the consequent change in the energy content of the capacity component of the spark) have but little effect on the incendivity of the spark. It will be borne in mind that the square of the primary current can be used as a measure of the total energy ($\frac{1}{2}Li^2$) in the spark, and the square of the gap width can be used as a measure of the energy ($\frac{1}{2}CV^2$) in the capacity component, the sparking voltage being proportional to the gap width within the small range of variation used in the experiment. It was found that with a gap width of 0·0135 in., a current of 1·5 amp. in the primary failed to produce an igniting spark, but on increasing the current to slightly over 1·6 amp. ignition was obtained. The effect of increasing the current was to increase the energy in the inductance component of the spark; it had no effect on the capacity component as the amount of energy in this component is determined solely by the sparking voltage and the distributed capacity associated with the secondary side of the spark-producing system.

After restoring the current to its original value of 1·5 amp. the gap width was increased until (with that current) an igniting spark was obtained. The amount of increase required was from 0·0135 to 0·014 in., a very small amount, but the result was quite definite. In this case the total energy in the spark was not changed. The effect of increasing the gap width was to transfer energy from the inductance to the capacity component.

The figures obtained enable a useful comparison to be made of the relative incendivities of the two parts of the spark in the conditions of this experiment. The increase of energy in the capacity component resulting from increase of spark width was in the ratio of 1 : 1·06. But the increase of total energy due to increase of current was in the ratio of 1 : 1·14. The difference in this example is not large, but it is definite and serves to show that the incendivity of the capacity component was greater than that of the inductance component.

The evidence of the experiments described above shows that the incendivity of a spark depends in part on the rate at which energy is dissipated by the spark, the incendivity of a capacity spark being greater than that of a *comparable* inductance spark dissipating the same amount of energy. The incendivity of both kinds of sparks depends, however, to an important extent on the dimensions of the spark and the configuration of the electrodes between which the spark occurs.

Ignition by Corona Discharge

By corona discharge is meant the glow which occurs in a gas at atmospheric or higher pressures in the region of a solid surface electrically charged to a sufficiently high potential. It was at one time believed that a corona discharge could not ignite an inflammable gas mixture. There is justification for this belief. Nevertheless, it is also true that a corona discharge can cause ignition. The fact that ignition can be so caused was established by the writer in the following experiment. A pair of pointed electrodes were arranged in an explosion chamber connected to an induction coil. The gap between the electrodes was such that a spark could not pass when the chamber was filled with air or with coal gas at atmospheric pressure, and the current in the primary winding of the coil was adjusted to a value at which a glow was produced on the points of the electrode. When the chamber was filled with an explosive coal gas-air mixture, the latter exploded after an interval of time which varied with the size of the gap. With a given mixture the time could be made to vary from a fraction of a second to as much as two minutes. If the gap was made too long no explosion occurred. When the flame appeared in the mixture a spark passed at once, and the sparking persisted for a second or more after the flame had vanished. The sparking appeared to be a consequence of the inflammation of the mixture and not the cause of it.

The subject of ignition by corona discharge has been systematically investigated by R. W. Sloane.[11] He found confirmation of both of the above statements. In some conditions he got ignition and in others he failed. His experiments were of two kinds in which transitory and sustained discharges

respectively were used. In the first, a pair of thin ebonite plates were charged by contact between a pair of brass plates connected to a Wimshurst machine. After charging the brass plates were removed and the ebonite plates separated, causing a discharge to occur. With this method he failed to get ignition of a coal gas-air mixture, although the discharges were both audible and visible. In another method, using transitory discharges he used a pair of brass rods arranged in alignment with a gap between their ends, and he enclosed the gap end of each rod by a sleeve of insulating material. The various materials used included paraffin wax, ebonite, glass, and different kinds of wood. The brass rods were connected to the poles of a Wimshurst machine. With a gap of from 1 to 10 mm. between the adjacent ends of the sleeves he was able to get a visible discharge across the gap excepting when sleeves of paraffin wax were used. The discharge failed to cause ignition of a coal gas-air mixture when it occurred between the ebonite or glass sleeves. Also no ignition was obtained with any of the wooden sleeves excepting sleeves made from lignum vitae, and then only when the gap was opened out to from 12 to 18 mm. At certain gap widths the wooden sleeves were punctured by the discharge, and in every case the resulting spark caused the gas to be ignited. When the experiments were repeated with glass sleeves heated to 100° C. the discharge across an 8 mm. gap resulted in ignition. The result was attributable to a sufficient lowering of the electrical resistance of the glass by heating. The energy of the discharge sufficient to cause ignition of a coal gas-air mixture between glass electrodes 5 mm. apart heated to 102° C. was 0·003 joules.

In the second series of experiments Sloane used electrodes made from slate rods. A steady high potential was maintained across the gap between the adjacent ends of the rods by a large induction coil acting through a large diode valve. In these experiments ignition of a coal gas-air mixture always resulted when the primary current of the induction coil was suitably adjusted. In a modification of these experiments small metal tips were attached to the adjacent ends of the slate rods to concentrate the discharge.

Sloane summarizes the results of his experiments thus:

"It was not found possible to ignite coal gas-air mixtures by the discharge of electricity between the surfaces of good insulators such as paraffin wax, ebonite, or cold glass. It is possible to ignite such mixtures by the discharge of electricity between the surfaces of less good insulators such as white fibre, glass at 100° C., or slate. A steady corona discharge between slate electrodes 3 or 4 mm. apart carrying a current of about 300 microamp. will ignite the most easily ignited coal gas-air mixture. The steady corona discharge between metal points 3 to 4 mm. apart will ignite the most easily ignited coal gas-air mixture when the current is greater than 300 microamp."

CHAPTER III

INFLAMMABILITY OF COMBUSTIBLE GAS AND DUST MIXTURES

It is a familiar fact that some combustible gas mixtures are more easily ignited than others. As extreme examples may be mentioned ether and oxygen, and dry carbon monoxide and air. The former can be ignited by a spark so weak as to be visible only in a darkened room. The other requires an exceptionally energetic spark. It is also well known that mixtures of the same constituents in different proportions require different amounts of spark energy for their ignition. The results of some measurements by R. V. Wheeler[12] on mixtures of certain paraffin hydrocarbons with air at atmospheric temperature and pressure are shown in Fig. 8. The sparks used were produced by an induction coil, and the primary current required to give the least igniting spark was used as the measure of spark energy. Curves of similar shapes are obtained when ignition is effected by pure capacity or pure inductance sparks or by small flames. Also curves of similar shapes are obtained with air mixtures of other gases such as coal gas, blast-furnace and producer gases, and petrol.

On inspection of any of the curves shown in Fig. 8 it will be seen that each of these tends towards a limit at each end. These limits are termed the "limits of inflammability." It is necessary to explain this term as its significance is sometimes misunderstood. If a sufficient spark is passed in any mixture lying within the limits of inflammability the flame initiated by the spark will travel throughout the whole of the gas in the containing chamber. Ignition can also be caused in a mixture lying outside either limit, but the resulting flame will not be capable of self-propagation throughout the whole of the gas, and will become extinguished at some distance from its source. A limit mixture is one which is only just capable of sustaining self-propagation of the flame initiated by a spark or other source. The limits of inflammability are characteristic

features, and they vary greatly with the nature of the constituents. So far as is known there appears to be a lower limit for all combustible gases, but the upper limit of a few gases

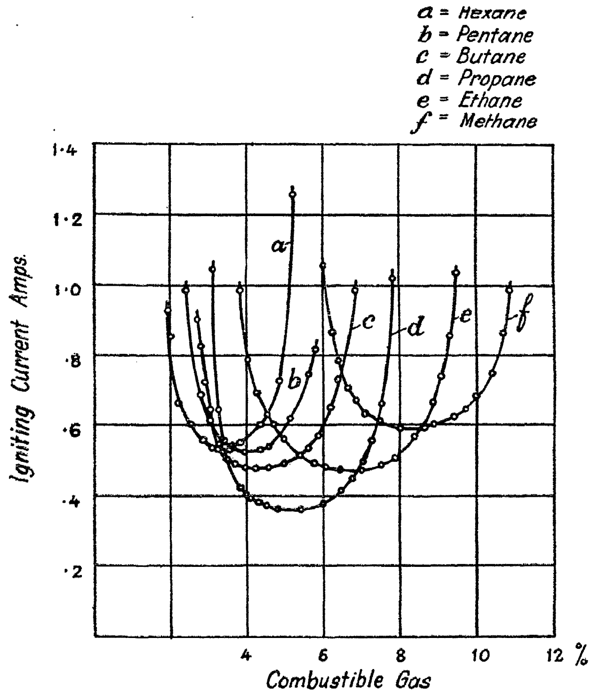

FIG. 8

appears to be indefinite. The approximate limits for some gas and air mixtures at atmosphere pressure and temperature are given in the table on the next page.(13)

The limits of inflammability are affected by several modifying influences. At atmospheric pressure and temperature they depend to some extent on the direction of travel of the flame from its source. Thus the limits found when the flame is caused to move downwardly in a vertical tube may be slightly different from those found when the flame is caused to move upwardly in the tube, or horizontally in a horizontal tube.

Gas or Vapour	Lower Limit by Volume (Per cent)	Upper Limit by Volume (Per cent)
Hydrogen	4·1	74
Hydrogen sulphide	4·3	46
Carbon disulphide	1·0	50
Carbon monoxide	12·5	74
Methane	5·3	14
Ethane	3·2	12·5
Propane	2·4	9·5
Butane	1·9	8·5
Pentane	1·45	7·5
Ethylene	3	29
Acetylene	3	—
Benzene	1·4	7
Methyl alcohol	7	—
Ethyl alcohol	4	19
Ethyl ether	1·7	26–48
Benzine	1·1	—
Petrol	1·5	6
Water gas	6·9	55–70
Natural gas	4·8	13·5
Coal gas	5·3	31
Blast-furnace gas	35	75

Other factors which affect the limits are temperature, pressure, and turbulence. For a full account of the subject of inflammability limits of gases and vapours and the conditions which influence them the reader is referred to Bulletin 279, by Coward and Jones, and issued by the U.S. Department of Commerce Bureau of Mines,[13] but a brief comment may be useful here on two prevalent misconceptions. It is sometimes said that a mixture lying outside either limit cannot be ignited. This is not correct. An extra-limit mixture can be ignited, but it will not sustain the flame. It is also sometimes said that a spark insufficient to cause ignition of any mixture has no effect. This also is not correct. Any spark will burn some of the gas in its immediate neighbourhood, but the amount may be very small. The fact that an insufficient spark causes some combustion provides a piece of evidence which is made use of in the thermal theory of ignition to be described in a later chapter. In some conditions a tiny flame can be seen around the spark. Otherwise the fact that some combustion has occurred is ascertained by the resulting fall of pressure or by

analysis of the gas after passing through it a succession of such sparks.

The inflammability of a gas mixture as measured by the amount of spark energy required to ignite it depends not only on its composition but also on its initial pressure. Examples are given in Fig. 9. Here are shown two curves respectively

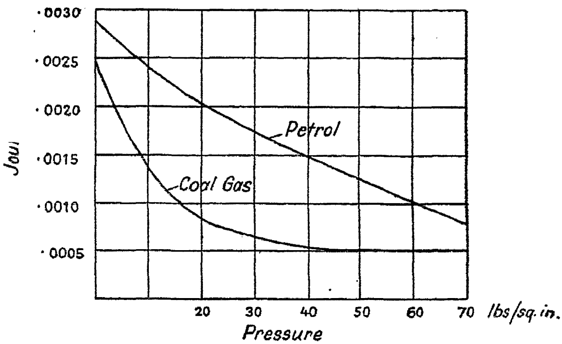

Fig. 9

relating to coal gas-air and petrol-air mixtures, and representing the relationship between the energy of the least igniting spark and the initial pressure of the mixture ignited. Ignition was effected by inductance sparks obtained by means of a "flick" interrupter as described in Chapter I (Fig. 3). For the coal gas curve a mixture of low inflammability was selected on account of the difficulty of measuring with sufficient accuracy the small amount of energy required to ignite the most inflammable mixture at the higher pressures. The petrol-air mixture used was one of nearly maximum inflammability, but as the writer could not be certain about the composition of the successive samples used in obtaining the results shown by the graph, this latter must not be interpreted as showing more than that the inflammability increases greatly with compression. The curves establish the important fact that inflammability increases with compression. Most gases appear to have the same characteristic. A curve obtained by R. V. Wheeler[(7)] from experiments on a 9·5 per cent methane-air mixture is shown in Fig. 10. In these experiments he used an induction

coil spark and noted the primary current required to produce the least igniting spark.

Turbulence appears to have a slight diminishing effect on inflammability in that it increases slightly the energy required in the least igniting spark. The difference obviously varies

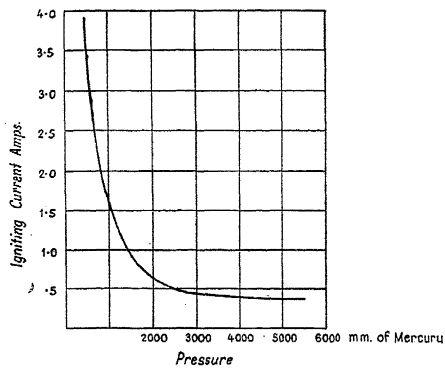

FIG. 10

with the degree of turbulence and no useful quantitative evidence can be given owing to the impossibility of ascertaining the motion of the gas in the immediate vicinity of the spark. Moreover, it is difficult to decide whether the effect of turbulence is to reduce the incendivity of the spark or quench the combustion initiated by the spark. In one of his experiments, R. V. Wheeler(14) used a fan within his explosion chamber. Ignition of an ethane-air mixture was obtained by means of an induction coil spark. The spark was more than sufficient to ignite any inflammable mixture of ethane-air when the mixture was still. Yet he found that "no ignition, or rather no propagation of flame," took place when the mixture was agitated by the fan running at 100 revolutions per second. On stopping the fan and allowing the turbulence to subside ignition took place readily with complete inflammation of the mixture. The chamber in which the experiment was performed was made of glass and consequently the occurrence of the spark and development of the flame could be seen. If the

experiment had been performed in an opaque vessel it would have been a reasonable inference that a spark capable of igniting a still mixture was incapable of igniting a turbulent mixture. But what Wheeler recorded was that he "found no ignition, or rather no propagation of flame," the suggestion being that there might have been ignition and that the resulting flame was quickly extinguished. The writer has not been able to form any very definite opinion on this point from his own work, though the evidence seemed to indicate that turbulence diminished slightly the inflammability of a gas to the extent of making irregular the ignition of a gas mixture by a spark capable of igniting with regularity the same mixture when still.

Ignition Temperature

This quantity resembles the spark energy required to ignite an inflammable gas mixture in that it varies with the means used for measuring it and the condition under which the apparatus is operated. For a full description of the various means used for ascertaining ignition temperature and particulars of the ignition temperatures of a large number of different gas mixtures, the reader is referred to the well-known work of Bone and Townend entitled *Flame and Combustion in Gases*.(15) For the writer's present purpose it is not necessary to describe any of these means (excepting two which will be mentioned later) as he is concerned only with drawing attention to certain factors that affect ignition temperature, namely, composition of mixture, pressure, and time (or lag). For some purposes the figure representing the ignition temperature of

MIXTURES OF GAS AND OXYGEN OR AIR
(*Proportions unspecified*)

Gas	Ignition Range (° C.)	
	Oxygen	Air
Hydrogen	580–590	580–590
Carbon monoxide	637–658	644–658
Ethylene	500–519	542–547
Methane	556–519	650–750
Ethane	520–630	520–630

a particular gas mixture is useless unless the pressure and lag are also specified. To elucidate the first point to be made it may be convenient to start with a list of the ignition temperatures of a few gases determined by Dixon and Coward (quoted from Bone and Townend).[15] (See table, page 33.)

It will be noticed that the ignition temperature for any

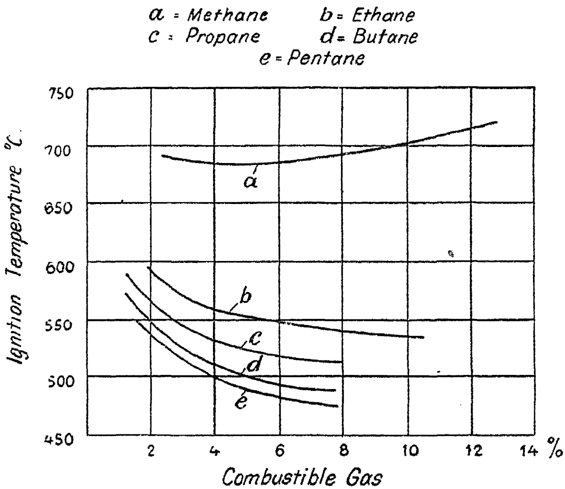

FIG. 11

particular mixture is not given as a single figure, but is expressed as a range. This implies that mixtures of the same constituents in different proportions have different ignition temperatures, and that as the mixtures used when making these measurements were indeterminate, the figures obtained in successive measurements were not all the same but fell within certain limits described as the range. To show that the composition of a mixture affects ignition temperature, some results obtained by Mason and Wheeler[16] are given in the graph at Fig. 11. The measurements were made in mixtures of the gases specified and air.

As will be seen in the table of ignition temperature ranges, the ignition temperatures of some gases are lower when mixed with oxygen than when mixed with air. This difference is

considerable in gases obtained by the volatilization of some fuel oils. For example, a Diesel engine oil which ignited at between 400–460° C. in air ignited at 350° C. in oxygen.

As to the next point it is important to know that the ignition temperature of a gas mixture is influenced by pressure, increase of pressure above that of the atmosphere being usually accompanied by decrease of ignition temperature. The following figures (Dixon) are examples[15]—

Mixture in Air	Time (sec.)	Ignition Temperature (° C.) (Atmospheres) 1	2	3	5	7
Hydrogen .	0·5	630	628	624	618	611
Methane .	0·6	746	—	705	675	653

In obtaining the figures tabulated under the heading "Ignition range," the time allowed for ignition to occur was indefinitely long, but in obtaining the figures relating to the effect of pressure the time in which ignition occurred was that specified. As regards hydrogen at 1 atmosphere pressure, the figure there given is higher than that given in the previous table, and as regards methane at 1 atmosphere pressure the figure is near the upper limit of the range given in the previous table. Both figures lead to a consideration of the third point, namely the effect of time on ignition temperature. Instead of "time" the term "lag" is more commonly used, and this is the term that will now be adopted. By lag is meant the time interval that elapses between the attainment by the mixture of the ignition temperature and the appearance of flame. When the ignition temperature is ascertained by admitting the gas mixture into a chamber already heated to a known temperature, the lag is measured by the interval which elapses between admission of the mixture and the appearance of flame, it being then assumed that the time occupied in heating the gas to the ignition temperature is negligibly short in comparison with the interval which elapses before the appearance of flame.

The lowest ignition temperature of any given gas mixture

is that found when the heating time is long. To obtain ignition within a shorter time the temperature of the heat source must usually be increased. The following tables (Dixon) serve to elucidate this statement.[15]

HYDROGEN AND AIR AT ATMOSPHERIC PRESSURE

Lag (secs.)	Ignition Temperature (° C.)
0·5	630
1·0	619
2·0	605
5·0	588

METHANE AND AIR AT ATMOSPHERIC PRESSURE

Lag (secs.)	Ignition Temperature (° C.)
0·6	746
1·0	728
2·0	710
3·0	694
10·0	657

When ignition is effected by an electric spark the ignition lag is negligibly small, this presumably being due mainly if not entirely to the relatively high temperature of the spark.

The fact that the temperature at which a gas mixture will ignite depends not only on the composition of the mixture but also on the pressure and the time available for ignition, is one of great practical importance, especially to those concerned with the use of liquid fuels in compression-ignition and other like engines. Whether turbulence affects ignition temperature does not appear to be very definitely known. It is reasonable to assume that it has a comparable effect to that on the spark energy required for ignition. In this connection the experiments by Paterson described in Chapter IV are interesting.

A well-known method of ascertaining the ignition temperature of a liquid fuel is that of dropping a small drop of the liquid into a heated metal crucible, the temperature of the interior of the crucible at which ignition occurs being the ignition temperature. In this method the interior of the crucible is at atmospheric pressure and time is not taken into account, the sole object being that of finding the lowest temperature at which ignition of a given sample can be obtained.

For the purpose of what follows, two figures obtained in this way by the writer will be quoted—

Diesel engine fuel, 360° C.
Petrol engine fuel, 420° C.

No absolute value is attached to these figures. They merely serve to effect comparison with other figures to be given later. The temperatures were measured by a thermo couple placed in the lower part of a small iron crucible heated by a Bunsen burner. It will be noticed that the ignition temperature of the petrol engine fuel is 60° above that of the Diesel engine fuel.

The ignition temperatures were then ascertained by a different method in which a definite time interval was introduced. The method will be described with reference to the diagram at Fig. 12. A glass tube (12 in. long and $\frac{3}{4}$ in. diameter) was

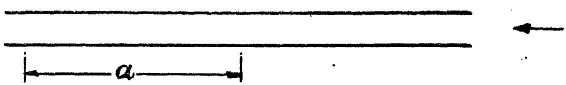

FIG. 12

heated along the region *a* (about 5 in. long) by a Bunsen burner. Both ends of the tube were open, and a thermo couple was placed in the heated portion. At the end indicated by the arrow a fine spray of the oil to be tested was blown from an air-atomizer. The latter was similar in principle to a scent spray, and was actuated by a small rubber bulb. The quantity of spray and air injected in each test was that which could be produced by a single squeeze of the bulb. The time interval occupied by the mixture in traversing the heated region of the bulb was small, though it was not actually measured. The temperature at which ignition occurred was given by the thermo couple. The figures obtained on the same samples as those used in the previous test were—

Diesel engine fuel, 620° C.
Petrol engine fuel, 570° C.

Here also no absolute value can be attached to the figures, but they are comparable with each other and with those already quoted. It will be noticed that both figures are higher than

the previous ones, due to the shorter time interval allowed for ignition, but the order of the figures is now reversed, that of the petrol engine fuel being 50° lower than that of the Diesel engine fuel. In the above experiments only the time interval was changed, and neither gives any indication of what result might be expected if the pressure were changed.

If the question at issue was the relative inflammability of different oils to be used in Diesel engines, where the ignition interval is very short, it might be inferred from the second figures that a petrol-air mixture would ignite more easily than the Diesel engine fuel, and that for the purpose of starting a cold engine, a petrol-air mixture would be more suitable. But this conclusion is at once negatived by a test on an engine in which the particular sample of Diesel oil fuel used in the above experiments ignited quite readily, whereas the petrol engine fuel used was incapable of ignition. Therefore it follows that when to the factor of time there is added the other factor, pressure, the results obtained in the second tests are again reversed, and that the figures obtained in the first two tests give no indication whatever of the relative inflammabilities of the two fuels in an engine in which ignition occurs under high pressure during a short time interval. As this point is of practical importance it will be re-stated in another way. Suppose that the ignition temperatures of a number of different fuel oils obtained in the usual way, at atmospheric pressure and with indefinitely long lag, are arranged in a descending (or ascending) series, *a*, *b*, *c*, *d*, . . . , then in the light of the above tests it cannot be assumed that the ignition temperature will be in the same sequence when ignition is caused to occur in a short time interval or at a high pressure.

The above simple experiments serve to show that to enable the inflammability of different engine fuel oils to be compared it is necessary when ascertaining ignition temperatures to take into account both lag and pressure. At the present time it appears to be generally agreed that the ignition temperatures obtained at atmospheric pressure and with long lag provide no satisfactory basis for the comparison of the inflammability of different engine fuel oils under working conditions, and it is now seen that a useful comparison can be made only when the

ignition temperatures are ascertained at the pressure and in the time interval which exist in an engine.

Ignition by Adiabatic Compression

Having regard to the last comment in the preceding section it would appear that an apparatus designed to effect ignition by adiabatic compression might meet the requirements of those concerned with fuels for Diesel, or compression ignition, engines, but this attractive alternative has its own difficulty. When a gas is heated by adiabatic compression the relation between the initial and final volumes and temperatures is given by the expression—

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

where T_1, T_2 are the absolute temperatures before and after ignition, V_1, V_2 are the corresponding volumes, and γ is a constant. In theory the constant γ is the ratio of the specific heat of the gases at constant pressure and constant volume. For air the figures commonly used are 1·4 or 1·39. In practice relating to engines and air compressors where the gas is subject to considerable cooling during compression, the figure is found to be in some cases as low as 1·3 or even 1·2. But from the point of view of the engineer concerned with ignition of a combustible gas mixture by compression in an engine, the lower figures, if true, may be misleading. Such a figure as 1·3 or 1·2 depends on the assumption that at a given instant during compression the whole of the gas is at the same temperature, and this may be erroneous. The portion of the gas in contact with the cylinder and piston may be and doubtless is cooler than the interior portion. When ignition is obtained by adiabatic compression inflammation begins at one or more points within the gas and not simultaneously at all points throughout the gas. This suggests a higher momentary temperature in some region or regions. And when it is remembered that the thermal conductivity of an iron cylinder may be about 3000 times greater than the conductivity of the gas contained within the cylinder, it is easy to believe that the mean temperature of the gas may be considerably below that of some hot

spot in the gas. As the evaluation of γ as ordinarily obtained is necessarily a mean value for the whole of the gas, it is possible that calculations based on it give no measure of the transient local temperature that may exist and that may be sufficient to start ignition. An adiabatic compression apparatus is an attractive practical means for ascertaining ignition temperatures under such conditions as those which exist in an engine, but until the enigma at present associated with the value of γ has been solved, the method can be used only for comparative purposes and cannot give a true measurement of ignition temperatures.

Ignition Accelerators

There is considerable interest in the search for substances which on addition to a mixture of fuel oil and air have the effect of lowering the normal ignition temperature. These additions are desirable when difficulty is experienced in starting a cold engine on a cold day. It is well known that traces of nitrogen peroxide have a large lowering effect on mixtures of hydrogen, carbon monoxide, methane, and ethylene. The following figures are given by Coward(17)—

Mixture in Air (0·5 sec. lag.)	Ignition Temperature (° C.)	Ignition Temperature (° C. with 0·5% NO_2)
Hydrogen . . .	About 625	About 455
Ethylene . . .	,, 625	,, 490
Carbon monoxide . .	,, 690	,, 610
Methane . . .	,, 725	,, 620

For comparison with the above it is important, however, to mention a fact which Coward(17) quotes from the work of Dixon. The latter found that the ignition temperature of a mixture of equal volumes of carbon disulphide and acetylene in air (520° C.) was higher than that of either carbon disulphide in air (150° C.) or acetylene in air (435° C.), and Egerton and Gates made a similar observation with a carbon disulphide-petrol mixture. The substitution of oxygen for air has but little effect on the ignition temperature of e.g. hydrogen or carbon monoxide mixtures, but it has a large effect on some mixtures

of which examples have already been quoted. Ethyl nitrate lowers the ignition temperatures and a trace of bromine or iodine increases the ignition temperatures of some mixtures. There appears no means of forecasting the effect on ignition temperature of adding a small quantity of an inflammable substance to an inflammable mixture, and when it is found necessary to assist the starting of a cold engine by the temporary use of a more readily inflammable substance than the normal fuel it is more advantageous to inject and ignite the temporary substance independently of the normal fuel than to inject the two as a mixture.

In an interesting experiment by Lewis and Kreutz[18] it was found that the passing of one of the constituents of a methane-air mixture through an electric spark prior to mixing and ignition had the effect of lowering the ignition temperature. The mixture consisted of methane, oxygen, and nitrogen, and these were brought together in separate streams. Before mixing, either the nitrogen or the oxygen was caused to flow through a condenser spark. In a test on a mixture containing 8 per cent methane it was found that "sparking" the nitrogen lowered the ignition temperature by 115° C., and sparking the oxygen lowered it by 233° C. This is a surprising result. Lewis and Kreutz attributed the result to the ionization residual in the gas after sparking, but a further comment will be made on this in Chapter IX.

Ignition of Liquid Fuels

Before a liquid fuel such as an oil of the paraffin series can be burned it must first be converted into a gas. Oil droplets do not burn as such. There is evidence for this in the burning of a candle. On looking at a lighted candle it will be seen that there is a region of gas between the wick and the flame, and the latter occupies the position at which the gas is mixed with sufficient air to enable combustion to occur. An experiment on this point is illustrated by Fig. 13. A test tube *a* has mounted in it a tube *b* having its lower end situated at a distance from the bottom of the test tube and having its upper end connected to an apparatus for inducing a gentle flow of air up the tube. The test tube is heated by a Bunsen burner to the so-called

ignition temperature of the oil, and in the bottom of the test tube is placed a single small drop *c* of, say, Diesel engine oil. The drop usually assumes the spheroidal state and is gradually evaporated. Ignition of the gasified oil does not occur in the immediate vicinity of the drop, but at a position near the lower end of the tube *b* where the mixing of the oil gas with air provides an inflammable mixture. This experiment is no doubt illustrative also of the mode of burning of oil in a furnace into which the oil is projected in the form of a spray.

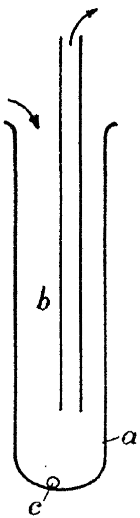

Fig. 13

In the gasification of oil drops it seems desirable to make them of as small a diameter as possible. When a single small drop is placed on the bottom of a test tube and heated, it is seen to evaporate slowly and the temperature must be raised to that of the boiling point of the least volatile constituent before the whole of the drop disappears. Moreover, when the drop is treated in this manner it usually leaves a stain on the tube. But when the oil is broken up into a fine spray in which the diameter of the droplets is of the order of 1 micron (0·001 mm.) rapid gasification occurs at a much lower temperature and without leaving a stain on the tube. This is an example of the well-known fact that if a drop of liquid of sufficiently low viscosity is reduced to a sufficiently small diameter it can no longer exist as such, even in a supersaturated atmosphere of its vapour. Certain specimens of Diesel engine oil are non-volatile at atmospheric temperature. When broken up by an air blast into a very fine spray or smoke in which the particles are sufficiently small to show Brownian movements under a microscope, the spray becomes gasified at a temperature of between 100–150° C., and no stain is left on the tube in which the spray is heated. But when a coarser spray is examined, this being produced by forcing the oil under pressure through a fine orifice with a swirling motion, a much higher temperature is required to gasify the spray and in the process a dark stain is deposited on the tube. The accumulation of a deposit of solid carbon

in a chamber in which oil is burned is no doubt mainly due to the oil droplets forming the spray being insufficiently small. Insufficient air will also cause carbon to be deposited. In general hard carbon deposit is due to coarseness of the spray. Soft carbon deposit is due to insufficient oxygen.

Inflammable Dust Clouds

Inflammable dust clouds have similar properties to gas mixtures and can be regarded as equivalent. Their inflammability depends on the nature of the dust, the smallness of the particles, and the ratio of dust to air. They can be ignited by sufficiently energetic sparks, flames, and hot solids, but usually the amounts of energy required to cause ignition are much greater than those required to ignite gas mixtures. Clouds of lycopodium, wood dust, sugar, starch, flour, sulphur, can easily be ignited by a small electrically heated coil of platinum wire. Coal dust is more difficult to ignite.

CHAPTER IV

IGNITION BY FLAMES, HOT METALS, RADIATION, AND IONIZATION

Ignition by Flames

SIZE, duration of contact with the mixture, and temperature are all factors that influence the incendivity of a flame, that is to say its ability to effect ignition. This statement is based on three important sets of experiments by different investigators. The first to be described are those by N. S. Walls and R. V. Wheeler.[19] In their experiments they used a vertical explosion chamber having at its upper end a cover in which was formed a hole giving access to the chamber, and in contact with the upper side of the cover was arranged a metal strip which could be moved at variable speed across the cover, the strip having a hole which could be moved across the one in the cover. Above the cover was mounted an inverted gas burner capable of projecting downwards through the holes in the strip and cover a small flame of variable length. The experiments were performed on methane-air mixtures, and the factors varied were length of flame, duration of contact of the flame with the gas mixture, and the composition of the mixture. The results are shown in Fig. 14. The curve marked *A* was obtained with a flame 1 cm. long and those marked *B* and *C* with flames 1·25 and 1·5 cm. long respectively. Each curve shows the relationship between the composition of the mixture and the time for which the flame had to remain in contact with the mixture to effect ignition. For the present purpose the interest in these curves centres in the fact that they establish the dependence of flame incendivity upon the size of the flame surface exposed to the mixture, and the duration of contact of the flame with the mixture.

The next series of experiments to be described are those by W. Rintoul and A. G. White,[20] on methane-air mixtures. In these a vertical explosion chamber was carried at one end of a horizontal rotary arm, and its open lower end was

supported on a fixed horizontal plate. In the plate was formed a slot, and beneath the slot was placed a Meker burner. When the arm was in motion it carried the explosion chamber through a circular orbit, and in each revolution the gas in the chamber was exposed for a short interval of time (dependent on the rate of rotation) to the burner flame. The size of the flame

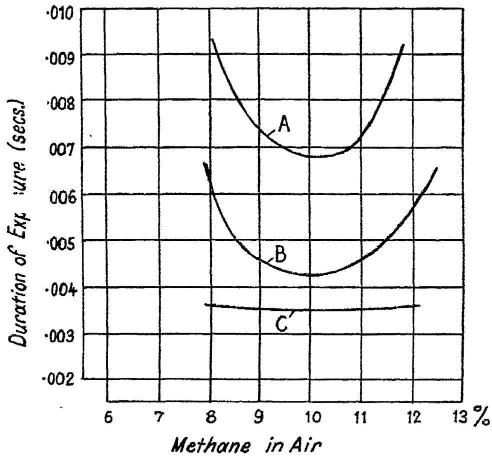

FIG. 14

was not varied, but its temperature was varied by appropriate adjustment of the composition of the gas mixture used in the burner. The results of the experiments are shown in Fig. 15. Here, also, each curve represents the relationship found between the composition of the mixture to be ignited and the duration of contact with the burner flame necessary for ignition. The different curves show the effect of varying the temperature of the igniting flame (the igniting flame temperature being indicated on each curve). These experiments establish the fact that the incendivity of a flame of fixed size depends on the temperature of the flame as well as on its duration of contact with the mixture to be ignited.

The third series of experiments are those performed by J. M. Holm[21, 22] on a variety of different gas mixtures, to ascertain the least size of flame capable of causing ignition.

His apparatus consisted of a vertical tubular explosion chamber closed at its upper end by a very thin (copper or mica) plate punctured by a small hole, or by a plug carrying a short metal or glass tube of small internal diameter. For the purpose of his experiments Holm made a series of thin plates with holes

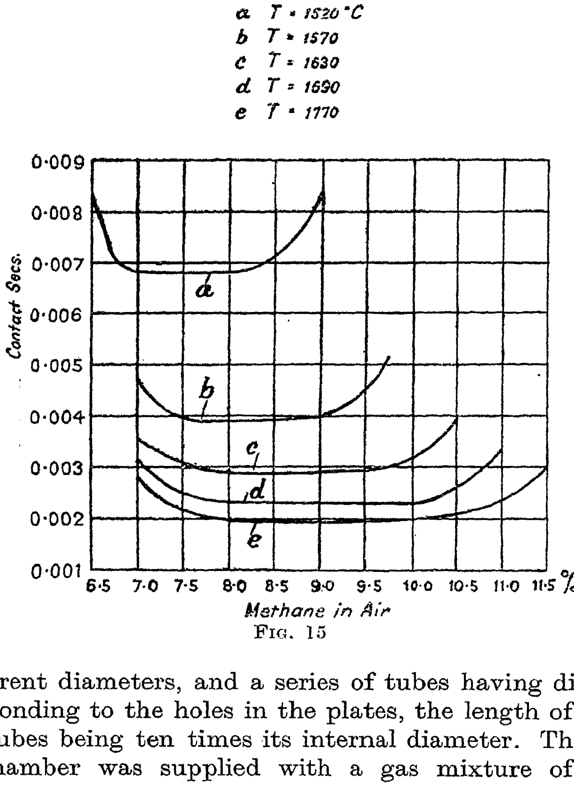

FIG. 15

of different diameters, and a series of tubes having diameters corresponding to the holes in the plates, the length of each of these tubes being ten times its internal diameter. The explosion chamber was supplied with a gas mixture of known composition from a storage vessel under the control of a needle valve whereby the rate of flow could be closely controlled. Having secured one of the plates on the top of the explosion chamber, and caused a stream of the gas mixture to flow slowly through the explosion chamber, the mixture escaping through the small hole in the plate was ignited. The

rate of flow was then gradually reduced by means of the needle valve. According to the size of the hole the flame then either passed through the hole and ignited the mixture in the explosion chamber, or went out abruptly on the top side of the plate without causing ignition in the chamber. In one example, when using a 20 per cent coal gas-air mixture, the flame went out on the top of the plate with all hole diameters up to 1·78 mm., but travelled through the hole and caused ignition in the explosion chamber with all hole diameters of 1·85 mm. and greater.

The rate of flow of the gas mixture through the hole in the plate was low and the flame formed on top of the plate was very small. The shape of the flame on the plate varied with the rate of flow. With a relatively high rate the shape was conical. On reducing the rate the flame assumed the form of a flat disc of slightly larger diameter than the hole. On still further reducing the rate, the under side of the flame assumed a hemispherical form of practically the same diameter as the hole. Having got the flame into the hemispherical form, further variation of the gas flow either resulted in extinction of the flame or in the passing of the flame through the hole into the explosion chamber where it caused ignition. It was found that the minimum diameter of hole through which ignition could be obtained was independent of whether the plate was of copper or mica. Also the experiments were repeated with gas-air mixtures of different compositions. In the other series of experiments the plates were replaced by the tubes.

Some of Holm's results with coal gas-air mixtures are represented by the curves in Fig. 16. Each curve shows the relationship between the limiting diameter of the hole or tube by which ignition could be obtained and the proportion of coal gas in the mixture. Curve *A* shows the results obtained with copper plates and curve *B* those obtained with copper tubes. Substantially similar results were obtained with mica plates and glass tubes. The curves shown in Fig. 17 represent results obtained with methane-air mixtures.

The above particulars are taken from the first of the two papers by Holm. In his second paper[22] he described an extension of his work with a variety of different experiments, and of these two will be briefly described. In one experiment he

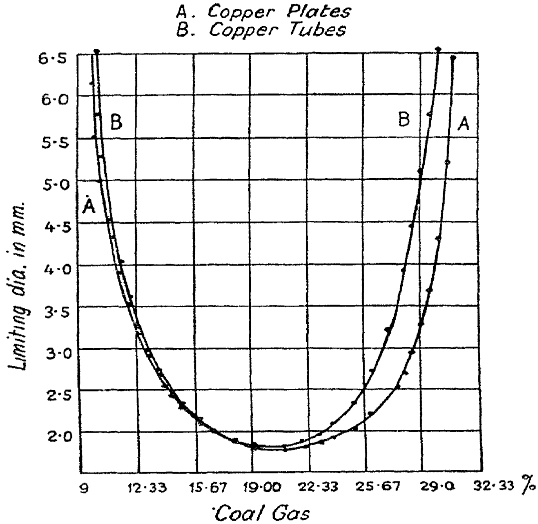
A. Copper Plates
B. Copper Tubes
Limiting dia. in mm.
6·5
6·0
5·5
5·0
4·5
4·0
3·5
3·0
2·5
2·0
A
B
9
12·33
15·67
19·00
22·33
25·67
29·0
32·33 %
Coal Gas

FIG. 16

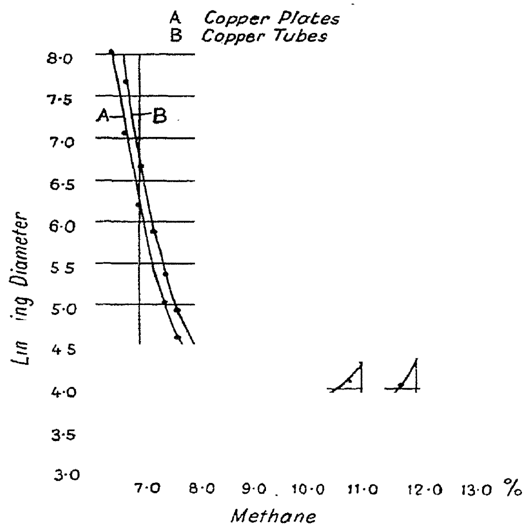
A Copper Plates
B Copper Tubes
8·0
7·5
7·0
6·5
6·0
5 5
5·0
4 5
4·0
3·5
3·0
7·0
8·0
9·0
10·0
11·0
12·0
13·0 %
Methane

FIG. 17

used a methane-oxygen mixture diluted with argon in the proportion in which nitrogen is present in a methane-air mixture, and he found that the flames would pass down tubes of smaller diameter than the flames of methane-air mixtures. The graph given by Holm is reproduced in Fig. 18. The supposition

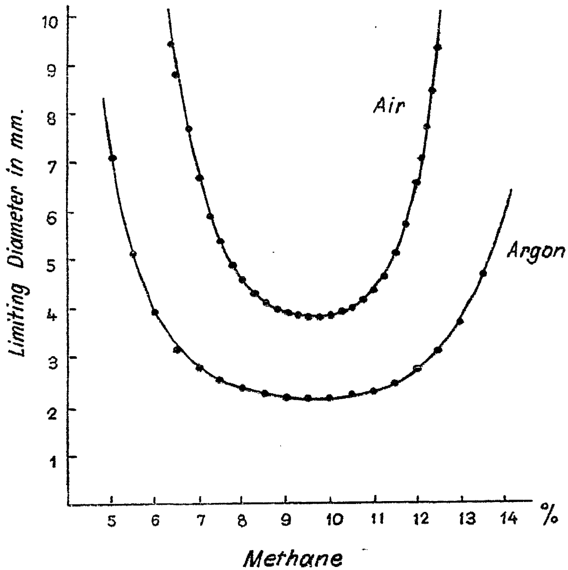

FIG. 18

underlying this experiment is that the extinction of a flame is controlled by the thermal properties of the gas mixture around the flame—thermal conductivity and specific heat being the two principal factors. Holm attributes the increased incendivity of the small flame obtained on replacing nitrogen by argon partly to reduction in the average thermal conductivity of the mixture and partly to reduction in the specific heat.

In another experiment he arranged a perforated partition at a central position in a vertical explosion chamber to determine the stopping effect of the partition on a flame started at the upper end of the chamber. The different partitions used consisted

of copper or mica plates each with a single hole or a group of holes, short lengths of copper or glass tubing, and gauzes made of iron wire or cotton threads. The results obtained were substantially similar to those obtained in the experiments first described. In commenting on the results obtained with iron wire gauze or cotton net Holm says "Over the most explosive part of the methane-air range (8·5–11·5 per cent) it appeared to be immaterial whether the gauze was made of iron wire or cotton thread, the size of the mesh and the diameter of the wire or thread being the important factors. For example, with a 9·5 per cent methane-air mixture the flame could just be prevented from igniting the remainder of the mixture by an iron gauze the meshes of which were squares with 2·72 mm. sides, the diameter of the wire being 0·46 mm., or by a cotton gauze having square meshes with 2·65 mm. sides and thread of thickness about 0·5 mm." Later on he says "the effectiveness of the partition in preventing propagation will be determined primarily by the size and spacing of its orifices, the thermal conductivity of its material being comparatively unimportant." Also "the extinction of the flame is due to the cooling effect of the unburnt gas in contact with its external surface, the limiting diameters being controlled by the thermal properties of the gaseous mixture."

Apart from his interesting work on the stopping power of perforated plates, gauzes, and tubes, the important fact established by Holm's work is that ignition of a gas mixture by a flame necessitates a flame of not less than a certain diameter.

Summarizing the above, the various experiments show that the incendivity of an igniting flame depends on its size, temperature, and duration of contact with the mixture to be ignited. Moreover, it depends on the cooling effect exerted on the flame by the mixture.

Ignition by Hot Solid Bodies

Here the subject enters a difficult and troublesome phase, as every experimenter knows who has worked in this field and has tried to find either regularity in his own results or agreement with the results of others. That a sufficiently hot solid will cause ignition of an inflammable gas mixture is, of

course, a fact of ordinary experience, and the experimenter may be forgiven for asserting in moments of despondency that that is about the only definite statement he can make on the subject. That ignition by a hot solid depends on temperature is obvious. But it also appears to depend on the material, the form of the material, and the condition of its surface, though as regards all these latter factors the experiences of different workers are confusing and contradictory. There is, however, general agreement that ignition by platinum—the material which is so convenient for use in ignition experiments—is anomalous, and cannot therefore be regarded as typical.

When surveying the divergent and perplexing results obtained by different investigators, a question that naturally jumps to the mind is this: Why is it that when the immediate object in view is to ascertain the ignition temperature of, say, a gasified oil, by means of a heated metal crucible, no difficulty is experienced in obtaining regular results, and that the results are such as to convince the experimenter that they represent the lowest temperatures at which ignition is possible at the pressure existing in the crucible, whereas ignition of the same mixture at the same pressure by, say, a heated wire surrounded by the mixture requires the heating of the wire to a much higher temperature than that to which the crucible was heated? The probable answer is that ignition in the crucible did not take place at the surface but was started at some region within the gas away from the surface, as in the experiment illustrated by Fig. 13, Chapter III. When the subject under consideration is that of ignition by a hot solid it is usually understood that the latter is surrounded by the mixture to be ignited and the mixture is free to flow to and from the surface by convection or otherwise.

Some indication of the perplexity associated with this aspect of the subject will be gathered from the following very brief account.

In a paper by W. Mason and R. V. Wheeler[23] results are given of experiments in which heated quartz vessels of different sizes were used for igniting different mixtures of methane and air. The results are shown in Fig. 19. The capacities of the vessels used are indicated on the curves. The lowest igniting

temperatures were obtained in the larger vessel. With reduction of the size of the vessel the ignition temperatures increased. The explanation of these differences is not easy, as neither

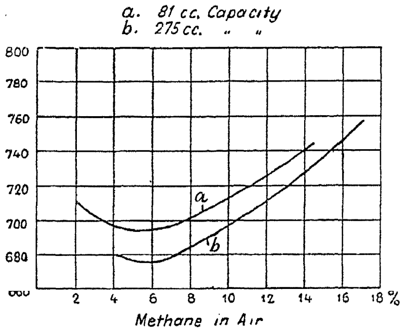

FIG. 19

catalytic action nor the relative cooling effects of the vessels appears to account for the difference observed.

When a heated metal body is immersed in an inflammable mixture ignition results only when the body is heated to a higher (and sometimes much higher) temperature than the normal (or lowest) ignition temperature of the mixture. This may be due to the fact that convection currents cause the time of contact between the mixture and the solid to be short, thereby necessitating the higher temperature always associated with a short lag. Or it may be that catalytic action is in some degree responsible.

The following comments extracted from Coward and Wheeler's "Safety in Mines Research Board Paper No. 53"(9) are informative. Metal bars will have to be much hotter to ignite the mixture that surrounds them than quartz tubes which enclose the mixture. A powerfully catalytic surface has to be far hotter to ignite an explosive mixture than has a surface of equal dimensions but of small catalytic action. When ignition of a methane-air mixture is effected by a heated metal bar a temperature greater than 1000° C. has to be exceeded to ignite even the most inflammable mixture of methane and air, this being some 300° C. higher than the

ignition temperatures of mixtures of methane and air enclosed in a quartz vessel. Turbulence imparted to the gas mixtures reduces the igniting temperature, provided the turbulence is not too violent. No bar of heated metal is capable of igniting methane unless its temperature is approaching 1000° C., that is, almost white heat. A red-hot metal bar would appear to be incapable of igniting methane. A wire, being smaller than a bar of equal length, will tend to have a shorter time of contact with a gas streaming around it, and so must be correspondingly hotter to provoke inflammation. Thick wires are more effective than thin wires of the same material, and gauzes are more effective than single wires in promoting inflammation. In certain experiments quoted by these authors it was impossible to obtain ignition of methane with any wire or gauze at a temperature of lower than 1000° C. They also quote an experiment by Thornton in which he failed to ignite methane with platinum wires at any temperature below their fusion point, though he readily succeeded with tungsten wires. Shepherd and Wheeler found that a platinum wire could be fused in an explosive methane air mixture without ignition if the heating current were slowly increased to the fusion point. Also no ignition was obtained when a current sufficient to fuse the wire rapidly was applied. Ignition was, however, obtained when a suitable current appreciably lower than the fusing current was suddenly switched through the wire, provided the diameter of the wire was not less than 0·1 mm.

In recent years some valuable experiments have been made by R. S. Silver and later by S. Paterson in the University of Glasgow, on the ignition of various gas mixtures by small solid spheres of different materials. This work carries the subject of ignition by hot solids out of the region of confusion into one of order and precision. In the experiments by Silver[24] spherical particles of platinum and quartz were heated in an electric furnace and projected therefrom by an air-blast through an explosion chamber containing the mixture to be ignited. The rate of motion of the particle was about 4 metres/sec. Particles of different sizes were used, ranging from 1·09 to 5·00 mm. diameter. The object of the experiments was to ascertain the temperatures to which the particles had

to be heated to effect ignition. Using a 10 per cent (Glasgow) coal gas-air mixture, he obtained the results shown in Fig. 20. In this graph sphere temperatures are plotted against sphere diameters. In the graph the black dots indicate the results obtained with platinum spheres and the crosses those obtained with quartz spheres. It will be noticed that both sets of results lie close to the curve, showing that the materials from which the spheres were made had but little influence on the results.

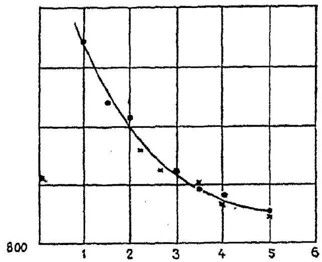

Fig. 20

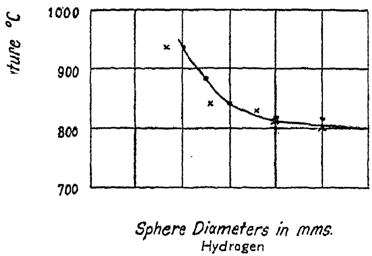

Fig. 21

A further important fact established by these experiments is that the smaller the sphere the higher was the temperature required to enable it to cause ignition. The temperatures recorded are all much higher than the normal ignition temperature of the mixture. Similar experiments were performed with a 20 per cent hydrogen-air mixture. The results are shown in Fig. 21. Here the results obtained with the quartz spheres (crosses) show a noticeable disparity from those obtained with the platinum spheres (black dots), suggesting that the results were to a greater extent than in the previous experiment influenced by the material of the spheres. Again the temperature to which the spheres had to be raised was much higher than the normal ignition temperature, which in this case was about 590° C.

Apart from their immediate results, these experiments help towards an understanding of the reason why fusion sparks are sometimes feeble igniting agents. Whilst it is a well-known and familiar fact that such sparks can ignite certain mixtures

(as, for example, in the ignition of coal gas or petrol vapour by the sparks given from pyrophoric materials), nevertheless a brilliant shower of fusion sparks obtained by rubbing together

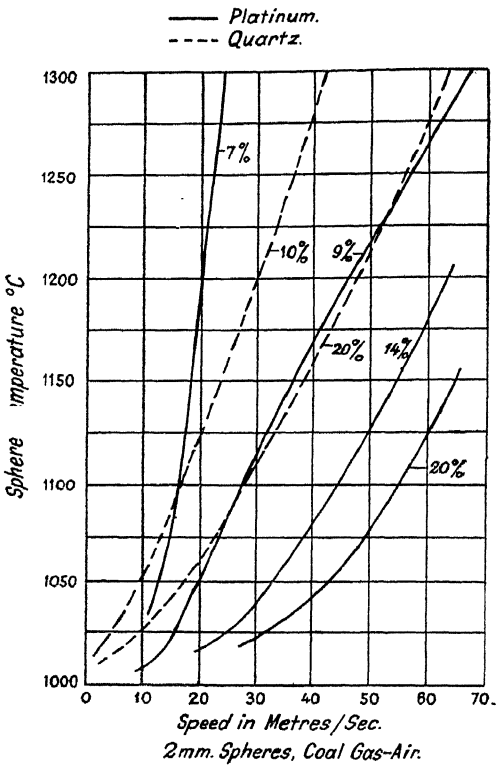

FIG. 22

a file and the end of a wire respectively connected to a small electric battery may fail to cause ignition. The Silver experiments show that the smaller the particle the higher must be its temperature to enable it to cause ignition, and unless the temperature of a tiny particle is high enough it will be ineffective. Later, work was carried out on similar lines by Paterson,[25] but with higher and lower rates of motion of the

spheres through the gas to be ignited. In some of his experiments he used spheres (of platinum and quartz) of 2 mm. diameter, and these were projected at different speeds through different mixtures of coal gas and air. A few of his results are represented by the curves in Fig. 22. These results show that

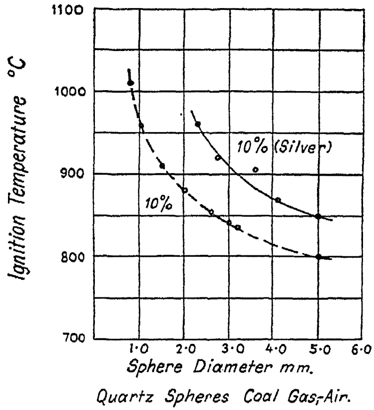

FIG. 23

different sphere temperatures are required to ignite different mixtures, and for the same mixture the temperature required increased rapidly with the speed of the sphere.

In a second series of experiments by Paterson(26) in which the spheres were dropped from a heater into an explosion chamber at a speed of 1·2 metres/sec., ignition was obtained at lower temperatures than in the first series. Also he found that the temperature required to cause ignition diminished with increase of the diameter of the spheres. One set of results obtained with quartz spheres in a 10 per cent coal gas-air mixture is shown in Fig. 23. The dotted-line curve represents Paterson's results, and (for comparison) the full-line curve represents Silver's results obtained at the higher speed of 4 metres/sec. Essentially similar results were obtained with other gas mixtures.

Paterson also ascertained the temperature to which spheres of different material had to be heated to effect ignition, the

spheres being of 2 mm. diameter and having a velocity of 1·2 metres/sec.

Some of his results are given in the following table—

Material of Sphere	10 per cent Hydrogen-air Mixture	10 per cent Coal Gas-air Mixture
	° C.	° C.
Platinum (old)	820	915
,, (polished)	> 875	> 1070
Nickel	815	900
Quartz	800	880
Porcelain	810	870
Slate	825	895

With the exception of that of platinum (polished) the figures are all of the same order of magnitude, showing that in the conditions of these experiments the temperature to which the spheres had to be heated to cause ignition was but little affected by the materials from which the spheres were made.

The experiments with heated spheres show that their incendivity depends on temperature, size, and duration of contact with the gas mixtures to be ignited. Moreover, these experiments show that, keeping other factors constant, reduction of size necessitates increase of temperature to cause ignition, and this fact, as already mentioned, helps towards a clearer understanding of ignition by fusion sparks.

Ignition of Solid Explosive Substances by Hot Wires

Much work has been done on ascertaining the kinds of ignition sources (spark, flames, and hot solids) that are capable of igniting inflammable dust clouds, but this work has had for its main object to determine what sources must be regarded as potentially dangerous in the presence of an accidentally formed dust cloud (as in a mine or factory), and though this work has been useful in achieving its immediate purpose, the writer is not aware of any results that can be regarded as having a scientific value in connection with the formulation of any theory of ignition. But certain experiments[(6)] on the ignition of explosive solid substances by hot wires have definite theoretical value and are worth recording here. The experiments

were made with the small fuse heads used in the electrical firing of explosives in mines. These articles are slightly larger in size than an ordinary match head and consist of a small quantity of a highly inflammable solid (a composition of copper acetylide and collodion) having embedded in it a short and thin

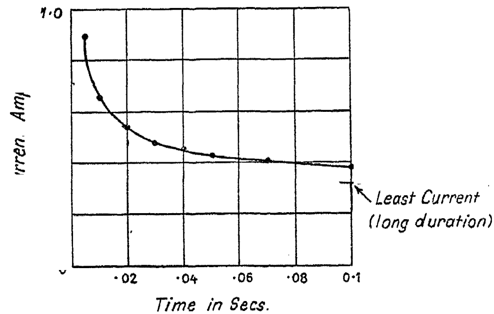

FIG. 24

metal wire. The ignition of the composition was effected by heating the wire by an electric current, and the purpose of the experiments was to ascertain how the least igniting current varied with the time for which the current was allowed to pass through the wire. The results of an experiment are shown in Fig. 24.

The results are also tabulated in the accompanying table, which includes not only the least igniting current and the duration of the current, but also the calculated value of the energy required to cause ignition, the energy being expressed by the quantity C^2rt, where C is the current in amps., r the resistance of the wire, and t the duration of the current in seconds.

Duration of Current (sec.)	Igniting Current (amp.)	Energy Required for Ignition (C^2rt)
—	0·32	—
0·1	0·38	0·0144
0·08	0·4	0·0128
0·06	0·415	0·0103
0·04	0·44	0·0077
0·03	0·48	0·0069
0·02	0·53	0·0056
0·01	0·66	0·0044
0·005	0·89	0·0040

The curve and table show that the shorter the duration of current the larger the current required to cause ignition. In other words, the larger the amount of current supplied the shorter is the time required for it to effect ignition. Moreover, the calculated figures show that the more rapid the rate at which the energy is supplied, the less is the amount of energy required for ignition. The results are similar to those obtained in the ignition of gas mixtures with sparks, flames, and solids, and, moreover, they serve well to exemplify the important fact that the effectiveness of a source of ignition depends on the rate at which it imparts its energy to the medium to be ignited—a fact of theoretical importance which will be dealt with more fully in the chapter on ignition theory.

Radiation

It is doubtful whether any fuel or mine gas mixture can be ignited by radiation of any kind. It has been suggested that ignition might be effected by passing X-rays through an inflammable gas mixture, but no conclusive experimental evidence has been found in support of the suggestion. Thornton[8] has stated that it is possible to ignite an explosive mixture by the incidence of X-rays on a platinum surface, but it is not clear whether the ignition resulted from the direct action of the rays, or from the heating of the platinum surface by the rays. It is hardly to be expected that radiation could cause ignition because of the transparency of the gases to radiation. In some experiments by the writer[27] a small coil of platinum mounted in an explosion chamber was heated by an electric current to the point at which slow reaction occurred in a coal gas-air mixture in the chamber. The current required to give the result was 0·56 amp., and the wire was not made visibly hot by this current. With a current of 0·54 amp. no reaction resulted. Then a needle situated with its point near the wire was charged by a Wimshurst machine. The voltage generated by the machine was sufficient to produce a faint glow on the needle point. With the current in the wire at 0·54 amp. no effect resulted in the gas from either the heat of the wire or the glow from the needle. But when (by allowing the Wimshurst to

discharge across an external gap) a sudden electrical impulse was produced at the needle point (the current in the wire being 0·54 amp.) reaction was started in the gas. With this lower current in the wire the reaction could be started only when an impulse was set up at the needle point. A steady voltage had no effect. It was already known from the work of Wynne-Williams[(28)] that when a needle is charged impulsively radiation is given off at the needle point, and this radiation (which has an ionizing action on air) belongs to that band of wavelengths lying between the ultra-violet and long-wave X-rays. The experiment appeared to suggest that the action of a wire heated to nearly the temperature at which it could start a reaction could be supplemented by a pulse of radiation. But the actions involved are very obscure, and if the experiment can be construed as giving evidence of the possibility of a chemical reaction being initiated by radiation, the evidence also shows that the effect is very small. In this connection an experiment described by Tchang Te-Lou[(29)] is interesting. A sparking plug having a gap of 4 mm. was fitted to an engine having a compression ratio of 5·5. Electrical energy was supplied to the plug from a magneto. With the gap width mentioned no spark occurred, the discharge being in the form of a corona. Ignition occurred with perfect regularity. The same engine was also operated with spark ignition, and comparison of powers obtained under the two conditions showed that where ignition was caused by the corona discharge a reduced power output was obtained corresponding to that which would have resulted by retarding the instant of ignition by a spark. In other words, to obtain the same power output under the two conditions it was necessary to over-advance the timing of ignition by the corona discharge. Tchang Te-Lou attributes the ignition by the corona discharge to ionization. But as it is improbable that ionization can cause ignition it is possible that the explanation of the result obtained is that each charge was heated by compression to a temperature near the ignition temperature, and that the heating of the charge in this way was sufficiently supplemented by a pulse of radiation for the gap to cause ignition, as in the writer's experiment above described. But it would be unwise on the basis of the

evidence available to form any definite conclusion on either of these experiments.

Ignition by Ionization

It is improbable that ionization of itself is capable of causing ignition. Sparks, corona flames, and hot solids are associated with copious ionization, and at one time it was thought that ionization might be a potent cause of ignition, but in recent years this supposition seems to have been abandoned. The writer has spent a good deal of time in trying to find evidence of ignition by ionization, but without success, and he is not aware of any experiment by others which supports the suggestion that ignition can be attributed either wholly or in part to ionization. There is, however, one possible condition which appears to give support to the suggestion that ionization may play a part in the ignition process. Where ignition occurs in a gas mixture at very low pressures (a few millimetres of mercury) and the mean free path of the molecules is relatively large, the speed of the translatory motions imparted by the field to ionized molecules may be comparable to that due to thermal motions of the molecules, and the speeds thus attained may be responsible for causing ignition. This point is more fully dealt with later in the chapter on ignition theory (page 125). At this stage it is sufficient to state that it cannot properly be cited as evidence of ignition by ionization. What is implicit in the suggestion that ionization is able to cause ignition is that the electrical charge on a molecule is (quite apart from any other condition associated with the molecule) capable of initiating reaction between the different molecules of the gas mixture, but this suggestion seems now to have been abandoned for lack of supporting evidence.

CHAPTER V

IGNITION IN ENGINES

It has already been explained that a high-tension magneto or induction coil spark normally has two components, a capacity and an inductance component. The latter component is not always present. If the current in the primary winding of the spark generator is only just sufficient to produce a spark at the plug, or if the insulation leakage associated with the plug or other part of the ignition system is sufficient to absorb that part of the energy that would otherwise appear in the inductance component, the spark will have only the capacity component.

An important practical question is whether ignition in an engine is attributable to the whole of the spark or only to the capacity component. Assuming that the magneto or coil and plug are of normal design, the answer to the question is that ignition is attributable solely to the capacity component when the spark occurs in a gas, but this answer may not be correct when the spark occurs in a fine mist or vapour such as an imperfectly gasified petrol-air mixture. As this answer is not yet unanimously accepted by those interested it is necessary to state the evidence on which it is based, but before doing so a certain preliminary explanation must be made. It is well known that the electrical insulation of sparking plugs (and indeed of parts of the high-tension side of the spark generator) is liable to vary under service conditions. Due to sooty deposits, excessive moisture when cold, or temporary deterioration of insulation when hot, electrical leakage often occurs over the surface of the plug insulations. Using a normal spark generator (magneto or coil) a considerable amount of insulation leakage at the plugs or elsewhere can be tolerated without interfering with the regular occurrence of the spark in the engine. The reason for this is that the energy supplied for the production of the spark is considerably in excess of that required to give only the capacity component. The surplus

energy under perfect insulation conditions would appear in the inductance component, giving the spark the "fat" or flame-like appearance so much desired by practical engineers. In the presence of considerable insulation leakage the surplus energy serves to ensure that at least the capacity component will appear at the plug, and under that condition, if the spark could be inspected, it would be found to have been shorn of some, if not all, of its fatness. This condition can readily be simulated in the laboratory by connecting a magneto or coil to, say, a well-insulated 5-mm. spark gap, and by connecting across the gap a leak in the form of a variable non-inductive resistance of a few megohms. Without the resistance the spark should present the characteristic appearance of a bright thin central core (capacity component) surrounded by an easily visible flame (inductance component). On bringing the resistance into action it provides an alternative path for the magneto or coil discharge and acts in the same way as an insulation leak. If the resistance is very high it will have very little effect on the inductance component and none on the capacity component, but on reducing the resistance gradually the inductance component will be seen to get less and less until it finally disappears. Now only the capacity component remains and a further diminution of the resistance will cause this to disappear suddenly. Incidentally it may be mentioned that this device has been used to measure what is termed the utility of the spark generator, the reciprocal of the resistance (in megohms) required to extinguish the spark at a standard gap being termed the "utility figure." When a magneto or induction coil is in service it has not only to provide the required spark at the plug but to do so in opposition to insulation leakage, and long before the reason was clearly understood the practical engineer had learned from experience that a spark generator giving a fat spark was more reliable in service than one giving a thin spark.

Insulation leakage at the plugs of an engine is a very variable quantity. Under good conditions it may be negligibly small. But when the engine is cold or very hot, or the plugs are covered with soot, the leakage may be high and in any of these conditions the inductance component of the spark may be very

small, if not non-existent. No evidence of this, however, will be manifest from the running of the engine so long as the leakage is not sufficient to cause spark suppression.

Reverting now to the main point under consideration, a simple test can be made to provide the basis for the answer above given. It is convenient to use a single-cylinder engine, fitted with a plug in good condition and connected to a magneto or coil capable of giving a fat spark. Across the plug is connected the variable non-inductive resistance. With the engine running in conjunction with any convenient dynamometer, the resistance is gradually reduced (thus simulating insulation leakage) until the spark is suppressed. Until the spark is suppressed no variation is observed in the power developed by the engine. It would appear to be unreasonable to attribute regularity of ignition to that part of the spark which is susceptible to large variation and may be non-existent, and it follows therefore that ignition must be attributed to the capacity component only. But the above is true only if the spark occurs in a gas. It may not be true if it occurs in an imperfectly gasified mist or vapour of liquid fuel and air.

It so happens (and this at one time was probably more a matter of accident than design) that the capacity component of the spark produced at a normal sparking plug gap by a magneto or coil of normal design is more than sufficient to effect ignition of any of the gas-air mixtures used in internal combustion engines. But before passing to the next point it may be relevant to mention a persistent misunderstanding of the statement that ignition in an engine is attributable solely to the capacity component. This statement does not assert that ignition cannot be caused by the inductance component, and yet that is how it is sometimes interpreted.

There remains another cause for the engineer's liking for a fat spark. In the early years of his career that distinguished authority on all matters connected with the design of ignition apparatus, Mr. E. A. Watson, constructed a small Wimshurst machine (in which the plates were enclosed in an atmosphere of desiccated compressed air) for effecting ignition on a motor cycle engine. He found that on cold days he had great difficulty in starting a cold engine, but when the engine was warm

ignition was quite satisfactory. On replacing the Wimshurst machine by a magneto giving a fat spark he had no difficulty in starting his cold engine on cold days. This experience caused Mr. Watson to believe that the inductance component of a spark was necessary to the process of ignition in a cold petrol-air mixture, and led the writer to re-examine the conclusion above mentioned.

Using an apparatus similar to that shown in Fig. 7, there was connected to the explosion chamber inlet a small air-blast atomizer (like a scent spray) containing petrol. The pressure in the explosion chamber was reduced by a vacuum pump and then air was allowed to flow in through the atomizer, carrying with it a rich charge of petrol. By suitably regulating the amount of reduction of pressure in the explosion chamber and keeping a constant level of petrol in the atomizer rich petrol-air mixture of sufficiently good uniformity could easily be obtained. The reason for adopting this procedure in preference to that of preparing a petrol-air mixture in a gas storage bottle was that it closely simulated engine conditions. The spark gap width and the primary current in the induction coil were adjusted to give a spark having an appreciable inductance component and just capable of causing regular ignition in successive tests with the condenser at zero, the spark being caused to pass immediately after the mixture had been introduced into the explosion chamber. Having obtained this set of conditions the capacity of the condenser was gradually increased, and it was found that on increasing the capacity sufficiently the spark failed to cause ignition of any of a number of successive charges. This result confirmed Mr. Watson's experience, and suggested that under the conditions of the experiment the incendivity of the inductance component was greater than that of the capacity component (the total spark energy being, of course, always the same). The method of carrying out the experiment was then slightly modified. The explosion chamber was slightly warmed, and after the mixture had been introduced it was allowed to stand for a short time before the spark was passed. A slight readjustment of the primary current was also made so as to obtain a spark that just failed to cause ignition with the condenser at zero. Then

on increasing the condenser capacity sufficiently it was found that ignition resulted, thus bringing the results back into line with the similar experiments on gas mixtures previously described. The explanation seems obvious. When a magneto or induction coil spark is passed through a mixture of air and imperfectly gasified petrol, that is to say, petrol in the condition of a mist of microscopic droplets, a part of the energy of the spark is utilized in gasifying the portion of the petrol in its immediate vicinity, a process which occupies a definite though short interval of time, and ignition is effected by what may be termed the tail-end of the spark. If in this condition the spark is of insufficient duration to effect gasification and ignition it fails to cause ignition. But when the petrol-air mixture is properly gasified, the sole duty of the spark is to cause ignition, and in that condition increase of the capacity component increases the incendivity of the spark, as in a methane, coal gas or other perfect gas mixture.

The above examination of the merits of a fat spark therefore results in this: In the first place the excess energy above that required to produce the capacity component is necessary to ensure the occurrence of at least the capacity component in the presence of insulation leakage. In the second place a spark having a large inductance component may serve to remedy the defects of the carburetting system of a petrol engine by gasifying sufficient vapour in its neighbourhood to enable ignition to occur.

When the gas mixture used in an engine is excessively rich or weak it may be that the capacity component of the spark is sometimes barely sufficient to cause ignition, and that in this condition the inductance component supplements the capacity component, but as, for the reason already given, the inductance component is variable and sometimes non-existent, and moreover as the capacity component is a more effective igniting agent than the inductance component, it is better to deal with an over-rich or weak mixture by increasing the gap width and so increasing the capacity component.

It has already been shown by the engine test (with artificial leak) above described that so long as a spark sufficient to ignite the gas occurs at the plug, increase of the total energy of the

spark has no effect on the power developed by the engine. This has been independently confirmed by a number of different investigators and is now generally accepted. Nevertheless there still persists among engineers a belief that the spark can in some way influence the manner in which an explosion develops in an engine cylinder such as by increasing the rate of development of the explosion pressure, or by setting up a tendency to pinking or detonation in an engine which with a different spark would not show that tendency. Such a belief cannot be dismissed as groundless, though it is probably wrong to attribute the results to the spark. Effects of this kind are often very difficult to reproduce and investigate in a laboratory, partly on account of the difficulty of ascertaining all the conditions that were present in the engine in which they were observed. In the early stages of the writer's work on the explosion of quiescent gas mixtures in a tubular explosion chamber having a sparking plug at one end and an optical pressure indicator at the other end, it was found that the time interval between the occurrence of the spark and the attainment of maximum pressure was sometimes affected when the plug was replaced by another of different design. Also, using an explosion chamber fitted with means for measuring the rate of flame movement along the tube from the spark, the speeds observed were very irregular (particularly during the first part of the travel of the flame) when the plug was of the kind ordinarily used in an engine such as that illustrated, for example, in Fig. 25. It will be noticed that between the insulation *a* carrying the central electrode *b* and the inner surface of the body *c* there is an annular space *d* which is of course filled with the same explosive gas mixture as that in the explosion chamber. The spark ignited not only the gas in front of it, but also the gas in the annular chamber in the plug, and the ignition of the latter gas caused a puff of flame to emerge from the plug and produce what has aptly been called by some engineers a "gun" effect, which appeared to accelerate irregularly the initial movement of the flame in the explosion chamber. This disturbing influence was removed by using a plug as shown in Fig. 26, in which a central electrode *a* was insulated from the inner end of the plug body *b* by insulation *c*, which

completely filled the space between the two parts, the spark occurring between the parts a, b across the end face of the insulation. Such a plug design is not suitable for use in an engine as it has been found to be very easily put out of action by sooty deposits, but for the purpose of the researches on

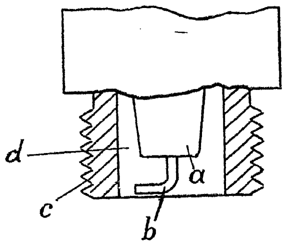

FIG. 25

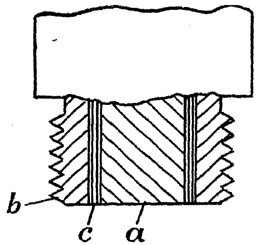

FIG. 26

which the writer was then working it completely removed the irregularities mentioned and enabled consistent results to be obtained in successive experiments. It may be (but this is only put forward as a suggestion) that the "gun" effect influences the performance of some engines, and if so the result is clearly not attributable to the spark but to the design of the plug. But evidence gleaned from engine tests does not seem to be very conclusive. In this connection it is also relevant to mention another experience. When using the plug shown in Fig. 26 at one end of a tubular explosion chamber it was found necessary that the flat end of the plug should be flush with the end face of the explosion chamber. When this end of the plug projected slightly into the chamber, or occupied a position in the plug socket behind the end face of the chamber, the flame movements under observation were erratic. Moreover, the following conditions in the explosion chamber also affected regularity of the rate of flame movement along the chamber, namely, corrosion of the chamber surface consequent upon continued use, the occurrence of a slight gap between the adjacent ends of a pair of tubes secured in alignment to form a chamber of the required length, and projections associated with the flame-speed measuring apparatus extending into the path of the flame. These are mentioned in support of the

suggestion that irregularities or undesired behaviour in the development of an explosion in an engine cylinder may be attributable to conditions associated with the cylinder. An improvement following on a change of plug may be due to the change of some factor associated with the plug, such as the position of the spark in relation to an adjacent portion of the cylinder wall, and not to the spark.

A remarkable and altogether exceptional experiment has been recorded by M. J. Burgess and R. V. Wheeler[30]. They ignited in a small glass globe an ethane-air mixture containing 3·5 per cent ethane. Using an ordinary induction coil spark the gas burned rapidly, but the flame movement could be followed by the eye. With a Wehnelt spark the mixture exploded violently, shattering the globe. The spark obtained when a Wehnelt interrupter was connected to the induction coil was, however, of an exceptional character. Current was supplied to the coil at 110 volts, and a flaming spark of large volume and great intensity resulted. In describing the experiment to the writer, Professor Wheeler said that the spark was comparable in size to the glass globe containing the gas. When the coil was operated with normal current, and the sparks were varied in length from 10–50 mm., no effect was observed in the subsequent inflammation. This experiment is interesting, but owing to the exceptional character of the spark it provides no ground for assuming that any of the sparks used in engines can influence the rate of development of the explosions initiated by them.

The persistence of the opinion that a spark can influence both the rate of development of the explosion pressure and the tendency to pinking or detonation warrants perhaps a further brief comment on each of these two points. What does influence the rate of development of the explosion pressure is not the spark itself (provided, of course, that this is sufficient to cause ignition), but the position of the spark in the combustion chamber, and no useful purpose is served by increasing the energy of an unsuitably-located spark in the hope that thereby the rate of development of the explosion pressure will be accelerated. This point will be made clear by a simple illustration. Suppose that the explosion chamber consists of

a tube two feet long and closed at each end, and suppose also that the sparking plug is situated at one end of the tube. The rate at which the flame will travel from the spark towards the opposite end of the tube depends on the nature of the gas mixture, and maximum pressure will be attained when the flame reaches the opposite end of the tube. If now the plug is transferred to a central position, where it is distant one foot from the two ends of the tube, the flame initiated by the spark will travel at equal speeds in opposite directions from the spark and the flame will fill the tube and maximum pressure will be attained in about one-half the previous time. Where (as is often the case in an engine) the combustion chamber is of irregular shape, it is not possible to determine from purely geometrical considerations the optimum position of the sparking plug, and this has to be settled either arbitrarily on the basis of previous experience, or by trial. It follows from the above consideration that there is another way of shortening the time interval between the passing of the spark and the attainment of maximum pressure, and that is by using two or more suitably separated sparks. Whether the gun effect above mentioned can be usefully employed for enabling the same result to be obtained from a single plug, or to neutralize the defect of a badly placed plug is a matter on which the evidence appears to be of a conflicting character. Moreover, it is conceivable that any gun effect capable of producing an appreciable result might introduce or aggravate a tendency to pinking. It must be mentioned, however, that this latter statement is based not on engine experience, but on experience with explosions in tubes, and it is therefore put forward only as a suggestion.

The conditions which give rise to pinking (sometimes called detonation) do not appear to be at all clearly understood by designers of engines, and there is need for a good deal of fundamental work of a rather difficult nature to be done on this subject. The rudimentary principles are, however, simple, but in the present state of knowledge they do not appear to be capable of such application to the design of a combustion chamber of complex form as to enable it to be said definitely that with a given fuel and position of sparking plug pinking will or will not occur.

There are two aspects to the problem of pinking, and they are concerned respectively with the fuel and the shape of the combustion chamber. The fuel chemists have attacked the problem with notable success, and it is probably true to say that engine designers have been content to allow the problem to be treated as one wholly belonging to the domain of fuel chemistry. On the other hand, engineers have gleaned from experience a large amount of information of an empirical kind which enables them to say that combustion chambers of some shapes are less liable to cause pinking than others, and that a tendency to pinking in a chamber of given shape can be minimized by placing the sparking plug in a particular position. To illustrate this point, the problem may be regarded as comparable to that of the designing of a church, theatre, or concert hall. At one time it was not possible to predetermine the acoustic properties of such a building, and success or failure depended largely if not entirely on the experience of the architect. Now, however, it is possible to predetermine with a large measure of success the acoustic properties of a building on a scientific basis.

In the writer's opinion it is probably true to say that the work of the fuel chemist can be frustrated by a badly designed combustion chamber, and that by a well-designed combustion chamber the work of the fuel chemist (so far as pinking is concerned) can be rendered unnecessary; though no doubt the joint efforts of both will always be required with the increasing demand for the generation of more and yet more power in an engine of given weight.

The approach to the problem of pinking on its physical side is best made by the study of explosions in a straight tube which is closed at each end, e.g. a tube of two inches diameter and one foot long, with a sparking plug at one end and an optical or other pressure indicator at the other end. The pressure-time diagrams obtained are usually of the general type shown in Fig. 27, which shows that the pressure rises gradually until it reaches the maximum, when the flame has completely filled the tube, and then falls. Tests made in such a tube with coal gas and methane-air mixtures (the first being a fast-burning gas and the other a relatively slow one) give diagrams

such as that shown in Fig. 27. On replacing the one-foot tube by a tube two feet long and repeating the experiment, the

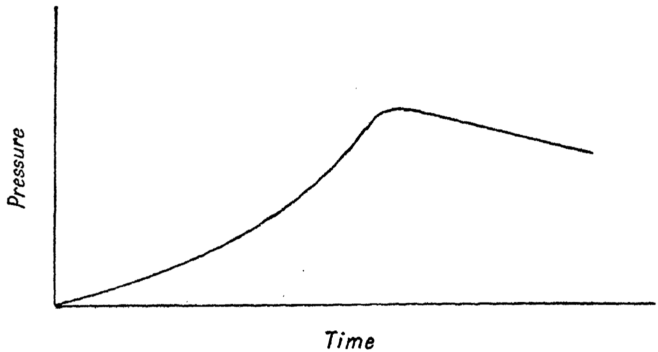

FIG. 27

diagrams obtained with methane-air mixtures are of the same character as those obtained with the one-foot tube. But those obtained with coal gas-air (if the mixture is one of maximum

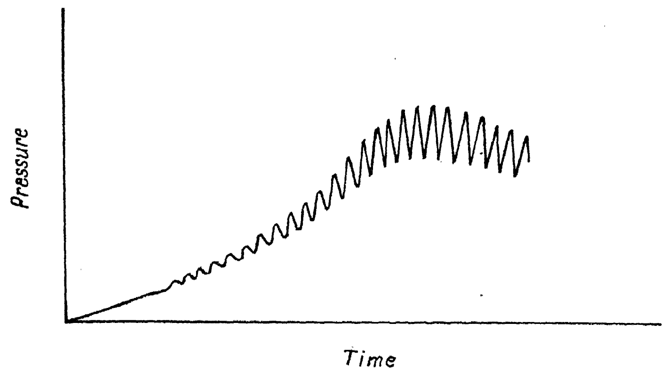

FIG. 28

inflammability in which the flame moves quickly) are of the kind shown in Fig. 28, and the explosion is accompanied by a characteristic metallic sound to which the word "pinking" is aptly applicable. The wave motion may vary from a gentle ripple beginning near the end of the flame movement to one

of great violence beginning gently very soon after the flame has started and ending with large amplitude at the end of the flame movement. On transferring the plug from one end of the two-foot tube to a side position at its centre, the character of the coal gas-air diagram changes. In some cases it was found that the vibrational motion was not present, but more usually it was present, though in less degree. It was also noticed in the course of experiments that slight corrosion in the inside of the steel tube used tended to accentuate the tendency to pinking. Thereafter care was taken to keep the interior of the tube clear and smooth. Later, Dr. W. A. Kirkby, at Sheffield University, found that when a sufficiently long tube (rather more than six feet) was used, the explosion of an 8·5 methane-air mixture was accompanied by pinking. (For further information on these experiments the interested reader is referred to the writer's papers mentioned in references [31] and [32].)

Photographic examination of the flame under conditions which result in pressure-time diagrams of the kind shown in Fig. 28 reveal that while the flame front is moving along the tube it is also vibrating, that is to say it is moving alternately backwards and forwards in the direction of motion. These vibrations sometimes attain large amplitude, and in the limiting condition the flame front shoots forward through the remaining unburnt gas at a very high speed, which is equal to that of a sound wave in the gas. It is this limiting condition which the scientist usually refers to as detonation, and it is doubtful whether it ever occurs in an engine cylinder, though the evidence on this point is not very definite, and some engineers assert that true detonation does sometimes occur in an engine. What is usually described as detonation or pinking in an engine is due to the vibratory condition of the flame front, and this may vary from a mild and harmless form to one which is violent and harmful. For further information on this subject the reader is referred to the work of Profs. H. B. Dixon, R. V. Wheeler, and W. A. Bone, and a brief survey is to be found in "Flame and Combustion in gases" by Bone and Townend.[15]

The two factors that appear to be responsible for pinking in the experiments above described are (1) rate of generation of heat in the flame front, and (2) the natural vibration frequency

of the gas column contained in the tube. When (1) is low and (2) is high no pinking occurs. When (1) is low, then (2) must also be low (as in a very long tube) for pinking to occur. When (1) is high, then (2) must be very high if pinking is to be avoided. The frequency of the vibration set up in a closed tube depends on where the source is placed. The frequency is lower when the sparking plug is situated at one end of a tube than when at the centre.

A simple and easy way of familiarizing the mind with the behaviour of vibratory bodies subjected to different impulsive forces, is to take a long spiral spring of thin wire suspended in a vertical position. On applying a gentle force to its lower end the spring can be extended uniformly without setting up longitudinal vibrations between the convolutions of the spring. But on applying a small force suddenly the spring not only extends but assumes a state of vibration the amplitude of which depends on the magnitude of the impulse. A column of gas in a tube is analogous to the spring, and the impulsive force applied to it depends on the rate of generation of heat in the flame. Pinking depends on suitable correlation of the above-mentioned factors (1) and (2), and the successful design of a combustion chamber (from the point of view of avoiding pinking) depends on the natural vibration frequency of the gas contained in the chamber being so high in relation to the rate of generation of heat that vibrations of large amplitude will not result. It will now be apparent that successful design depends on a knowledge of the acoustic properties of small closed chambers of irregular shape, and on this aspect of the subject very little if any useful information exists. But in any case, so far as the writer has been able to ascertain, the spark itself is not a factor in causing pinking, though its position in the combustion chamber may be and often is.

The writer is indebted to Professor E. Taylor-Jones for the following expression which was given by the late Lord Rayleigh and may prove to be of value to those who wish to approach the study of vibrational motion in gases on its mathematical side.

$$u = \frac{1}{n}\int_0^t \varepsilon^{\frac{1}{2}k(t-t^1)} \sin u(t-t^1)Udt^1$$

It represents the displacement u at time t of an oscillatory system (frequency n, damping factor k) produced by a force U acting over the time from 0 to t^1. If the total impulse $\int U dt^1$ is given and if the damping factor k is small, the expression has its greatest value when t^1 is very small, and t is such that sin $(t - t^1)$ is approximately equal to 1, that is, nearly a quarter period after the delivery of the impulse. The physical meaning is that under a given impulse an oscillating system has the greatest possible amplitude of vibration set up in it when the impulse is delivered as suddenly as possible.

Pre-ignition

It is generally believed that the presence of an incandescent solid, such as a red-hot sparking plug electrode, or a piece of glowing carbon, in an engine cylinder will necessarily cause pre-ignition. It is true that if an incandescent surface presents a sufficiently large area to the gas mixture, pre-ignition, that is to say, ignition which precedes the spark, can occur. But it is possible for an incandescent solid to be present without causing pre-ignition. It is probable, when the plug has a sparking electrode made from very thin wire, that this electrode is usually in an incandescent condition while the engine is in action, and it is known that plugs having thin wire sparking electrodes which become incandescent in the engine will operate normally, the ignition being due to the sparks and not to the hot electrodes. On cutting out the sparks, the engine may continue to run, but as if the instant of ignition had been greatly retarded. This is due to the fact that ignition by a hot solid is associated with a considerable time lag, and when an engine is running sufficiently fast, the lag involved may be such that ignition is effected only by the spark. There appear to be two possible diagnoses of pre-ignition. When an engine gets so hot as to cause incandescence of some part of the sparking plug, this condition may not become evident until the plug insulation (temporarily) fails and prevents the occurrence of the spark. The engine may then run for a short time with diminished speed due to ignition by the hot part of the plug. When the speed falls so low that the time of contact of the fuel entering the engine is comparable with the ignition

lag, ignition occurs during the early part of the compression stroke and the engine is brought to rest. It is easy to understand why, in this condition, the known device of replacing the plug by one of different design may overcome the tendency to pre-ignition, as it may be that the new plug is better able to get rid of its heat and so avoid its insulated electrode becoming incandescent, or the insulation may be able to withstand higher temperatures and so enable the sparking to persist. The other condition that may give rise to pre-ignition is the presence of a sufficiently large and sufficiently hot body in the engine, such as an overheated exhaust valve. With this the lag may be so short that as soon as the appropriate temperature is reached pre-ignition occurs, and the engine is quickly brought to a standstill.

The point intended to be brought out in the above comments on pre-ignition is that the presence of an incandescent solid in an engine will not of necessity cause pre-ignition. The time lag associated with spark ignition is negligibly small, but that associated with an incandescent solid may be sufficiently long to make it impossible for it to effect ignition during the time available in a fast-running engine. Lag depends both on the temperature of the incandescent solid and the area which it presents to the gas mixture, and pre-ignition can occur only when the one is sufficiently high and the other sufficiently large, or when the engine is running at a sufficiently low rate to enable the incandescent solid to take effect.

Ignition in Compression Ignition Engines

Here ignition depends on the temperature attained by rapid compression of the gas contained in the engine cylinder. The attainment of the necessary temperature when starting a cold engine is often a matter of difficulty, particularly in very cold weather. As explained in Chapter III, ignition by compression does not commence simultaneously in all parts of the gas mixture, but only at one or more localized regions. This suggests that the requisite temperature exists only at those regions. The temperature resulting from compression is very much less than that associated with an electric spark. Consequently, whereas consideration of ignition lag is of no

practical importance in spark ignition, it is of great importance in compression ignition. For reasons explained in Chapter III, knowledge of the least ignition temperature of a given gas mixture at atmospheric pressure and temperature with indefinitely long lag provides no guide to the temperature required to be produced at high pressure and where the permissible lag is short. As the engine designer appears to have (at present) no useful knowledge of what localized temperatures are attained in his engine, the suitability of a given fuel for a particular engine is a matter which can be settled only by trial.

To facilitate the starting of a cold engine various expedients have been adopted. Sometimes a glowing piece of tow or a cartridge of easily combustible material is inserted in the engine cylinder, or an easily ignitable liquid is injected with the normal fuel. In the latter case experience seems to show that it is better to introduce the two liquids separately and not as a mixture. A method sometimes resorted to is that of holding a torch of glowing tow or a lighted taper at the air inlet of the engine. The mode of operation of this expedient is not clear. It is said that it depends on the carrying of very fine particles of carbon into the engine cylinder which become incandescent under the heat of compression in the cylinder and provide nuclei at which flame can originate. The importance of the question of the ignition temperatures of liquid fuels for compression ignition engines is apparent, and judging from the present state of knowledge it would appear that much work remains to be done on this question.

CHAPTER VI

SPARK GAPS

THE subject of spark gaps is not directly relevant to the subject of this book, but as the two are closely allied a short description of some of the chief properties of such gaps may be useful.

The voltage required to produce a spark between a pair of electrodes depends primarily on the width of the gap between them, the shape of the adjacent electrode surfaces, and the pressure of the air or other gas in which the electrodes are located. There is a lower limit of voltage (about 300) below which a spark cannot be caused to jump a gap. The material of the electrodes has little or no effect on sparking voltage, but the nature of the gas has some effect.

The sparking voltage also depends in many instances on the manner in which the voltage is applied, being least when the voltage is applied steadily, as by a battery, a Wimshurst machine, or a high-tension direct current generator. This voltage is conveniently termed the nominal sparking voltage. When the voltage is applied impulsively, that is to say, suddenly and for a short time interval, as by an induction coil, the sparking voltage is usually a little higher and is sometimes much higher than the nominal. The ratio of these two voltages is termed the impulse ratio.

Impulse ratio depends largely on the shape of the gap electrodes, the width of the gap, and the gas pressure. It is usually least (and nearly unity) in a gap between spherical electrodes whose diameter is considerably larger than the width of the gap, or in an annular and suitably proportioned gap between a rod and a ring. It is greatest between needle points, when it may reach a figure of 2 or more. Impulse ratio also depends on the rate at which the applied voltage rises, being greatest when the voltage is applied with great suddenness as by a magneto or an induction coil. When the voltage is applied by an alternating current generator having a frequency of,

say, 50 periods per second, the peak value of the voltage wave required to produce a spark does not differ greatly from that of a steadily applied voltage. It is only when the voltage is applied very suddenly and for a short time interval that the condition associated with the term impulse ratio becomes very apparent.

The reason why the sparking voltage when applied impulsively is higher than the nominal or steady sparking voltage is that the gas in the gap is initially a good insulator and must be converted into a good conductor before the spark can occur. The process of conversion is one which involves ionization of the gas in the gap. Ordinarily the air of a room contains a few ions and it is the presence of these fortuitous ions that ordinarily makes sparking possible. When ions are absent sparking becomes difficult even at voltages greatly above the nominal sparking voltage. This fact, until it was recognized, was responsible for a good deal of trouble to makers of magnetos, induction coils, and sparking plugs, and as it provides a convenient approach to the study of the action of a spark gap from a practical point of view it may be worth while to describe an actual experience of many years ago.

At one time when subjecting a magneto to an endurance test it was usual to employ an ordinary engine sparking plug secured to a small chamber charged with air at a pressure of 80 lb. per square inch, the chamber being provided with a window through which the sparking at the plug electrodes could be seen. It was required that the magneto connected to the plug should be able to maintain regular sparking under this condition over a specified period of hours. In some tests it was noticed that after about an hour from the commencement of the test the sparking, which was previously quite regular, became irregular and eventually ceased. Quite naturally the magneto was rejected, despite the fact that no constructional defect could be found in it. As little was known among engineers at that time about spark gaps, and as there was no obvious reason why a spark gap should apparently misbehave itself, much fruitless effort was expended in a search for a possible defect in the magneto. But on one occasion it was accidentally discovered during a test of this kind when the

sparking had ceased that normal sparking could be restored by putting fresh air into the chamber. The full significance of this (at that time inexplicable) fact was not learnt at once. It was of course suspected that the result might have some connection with the state of ionization of the air, but seeing that the spark itself is so highly ionized, the question arose as to why the sparks did not maintain an adequate state of ionization in the chamber. Actually, after a spark has passed it leaves behind it little or no trace of ionization. It is perhaps important to stress this fact, because the belief is still held by some that a spark is an effective means of producing ionization in a chamber where ionization is required. The fact that ionization does not persist after a spark has passed can very easily be demonstrated by means of a gap connected to an induction coil having its primary winding controlled by a trembler-interrupter, the current in the primary winding, or the gap being so adjusted that sparking just fails to occur at the gap. When an ionizing agent such as a match flame or an insulated needle point is brought into the vicinity of the gap, sparks occur in perfectly regular succession at a rate dependent, of course, on the rate of vibration of the trembler. On removing the ionizing agent sparking ceases instantly. If there had been but little residual ionization in the gap during the interval between successive sparks, regular sparking would have been maintained. In fact, the succession is maintained only so long as the ionizing agent is present.

Before a spark can pass some ionization must exist in the gap and the process of preparing the spark path will now be considered. By common consent (following the well-known Townsend theory) there must be present in the gap at least one electron. Suppose for the sake of simplicity of explanation this is situated at the middle of the gap. Under the action of the electrostatic field in the gap it will move towards the positive electrode. Before it has travelled far it will on collision with a molecule (assuming, of course, that the field is sufficiently strong and the electron is therefore moving with sufficiently high velocity) expel an electron, leaving the molecule positively electrified. The new electron will behave like the first and in this way a vast number of electrons will quickly be produced.

The electrons will all swarm towards the positive electrode, and at the same time the positively charged molecules or ions from which electrons have been expelled will swarm towards the negative electrode. Eventually the positive ions will extend right across the gap, but before the discharge can assume the character of a spark, the electrons or negative ions must also extend right across the gap. As the first electron was supposedly at the middle of the gap and as all the electrons move in the one direction, the electrons in this example are to be found only in one half of the gap, and the question arises as to how the other half is filled up. According to the Townsend theory, the positive ions, in moving towards the negative electrode, also produce electrons by collision with the gas molecules, but for many years this part of the Townsend theory has been the subject of much controversy, as no satisfactory evidence of ionization by the collision of positive ions with gas molecules under conditions which occur in a spark gap has been adduced. The original Townsend theory has in consequence been modified slightly with the accumulation of additional knowledge of what happens in a spark path, and the authorities on this subject appear to be in a large measure of agreement that the positive ions play no part whatever in completing the preparation of the spark path. Any one or more of several possible actions resulting from the electron collisions may serve to complete the path, but in a gas at about atmospheric or higher pressure, the probability seems to be confined to either or both of two actions. They are the direct ionizing of the gas by a short-wave radiation resulting from the electron collisions, or the detachment of electrons from the negative electrode by such radiation. It is difficult to decide between these alternatives as both may be operative, but the fact that the responsiveness of a gap when an insulated needle point is used as the artificial ionizing agent depends to some extent on the condition of the negative electrode suggests that the second of the two actions is the more potent.

The assertion that positive ions are inoperative is usually based on indirect evidence, but in the writer's opinion the fact is capable of direct demonstration by the following experiment, which makes use of the condition that the impulsive sparking

voltage of a gap is higher than the nominal sparking voltage, and that when the voltage is impulsively applied the passage of the spark can be facilitated by artificial ionization. The apparatus used by him is illustrated by the diagram at Fig. 29.

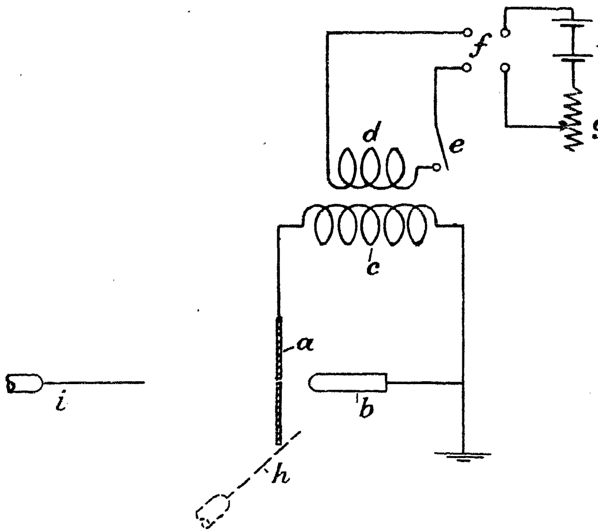

FIG. 29

An insulated thin brass disc *a* of about 5 cm. diameter has a tiny hole at its centre. In front and on the axis of the disc is mounted an earthed brass rod *b* of about 5 mm. diameter, and having a hemispherical end facing the disc. The width of the gap between the rod and disc is about 2·5 mm. The disc and rod are connected to the terminals of the secondary winding *c* of a small induction coil, and the primary *d* of the latter, which is connected to a 4-volt battery, is controlled by a vibratory interrupter *e*. A reversing switch *f* serves to control the direction of current through the primary winding *d*. A variable resistance *g* enables the primary current to be suitably regulated. The adjustment (effected by varying the primary current or the width of the gap) is such that sparking just fails to occur. The proper state of adjustment can readily be

ascertained by placing in contact with the edge of the disc a fine sewing needle *h* (shown in dotted lines) carried by an insulating handle and so situated that the point of the needle can "see" the gap. Having made the adjustment, the needle is removed and fixed at any convenient position behind the disc as indicated by *i*. It may be placed on the axis of the disc at a distance of an inch or two away, but this is immaterial. In a dry atmosphere it is sometimes effective at a distance of nearly two feet away from the back of the disc. The needle is then connected to the negative pole of a Wimshurst machine. With the induction coil in action and the disc negatively electrified, a very slight charging of the needle by the Wimshurst machine is sufficient to cause perfectly regular sparking at the gap between the disc and rod. As soon as the needle is withdrawn or the Wimshurst machine stopped, or a shutter is placed across the back of the disc, sparking ceases. The explanation of this effect is that electrons or negative ions pass from the needle through the hole in the disc and so cause the required initial ionization of the gap. On reversing the action of the induction coil so that the disc is now positively electrified, and on connecting the needle to the positive pole of the Wimshurst machine, no sparking occurs, showing that the positive ions which enter the gap through the hole have no effect.

Reverting now to the consideration of sparks produced by impulsive voltages, it will easily be understood that as the spark path must be prepared before the spark can pass, some short time must elapse between the attainment of the nominal sparking voltage and the occurrence of the spark, and during this time the voltage continues to rise. The extent to which it will rise depends on the time required to prepare the path and also on the rate at which the voltage is rising. The effect of an artificial ionizing agent is to accelerate the preparation of the spark path, and thereby minimize the impulse ratio. It cannot and does not lower the nominal sparking voltage of the gap.

The gap can be artificially ionized in a variety of ways. For demonstration purposes a match flame held below the gap, but not sufficiently near to affect materially the temperature

of the gas in the gap, is effective. Professor E. Taylor-Jones used in his well-known researches on the induction coil a gap in which a speck of radium was lodged in a tiny hole at the centre of one of his gap electrodes. By this device he was able to ensure a low impulse ratio and great uniformity in the action of the gap used by him in making impulsive voltage

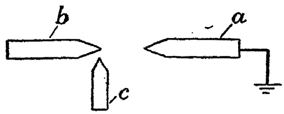

FIG. 30

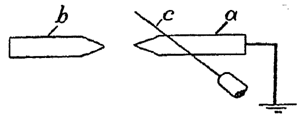

FIG. 31

measurements. A very well-known form of gap at one time extensively used in testing magnetos and ignition coils is that known as the three-point gap. This is illustrated at Fig. 30. It consists of two main bluntly pointed electrodes, one of which, *a*, is earthed and the other, *b*, is insulated, and adjacent to *b* is arranged a similar third point *c* carried by an insulating support, with its point near and slightly behind the point of *b*. When *b* is electrified a faintly visible and momentary discharge occurs between *b* and *c* immediately prior to the passage of the spark between *b* and *a*, and the effect of this discharge is to ionize the gap, so reducing the otherwise large impulse ratio and enabling regularity to be obtained in the sparking voltage of the gap.

An equally good result can be obtained by placing a sewing needle in contact with either electrode as shown in Fig. 31. The adjacent end of the electrodes *a*, *b* can be of any shape, and the needle *c* is so placed in contact with either electrode that whilst its point is opposite the gap it is also far enough away from the gap to prevent the spark from jumping to it.

The action of the two devices above described was not properly understood until it was elucidated by Wynne-Williams.[(28)] He showed that the effect is due to radiation from the discharge between *b*, *c* (Fig. 30) and from the point of the needle *c* (Fig. 31). He concluded that this radiation has the effect of directly ionizing the gas in the gap. For a fuller account of this interesting subject the reader is referred

to the original paper by Wynne-Williams,[28] and to later papers by J. Thomson[33] and the writer.[34]

From the point of view of those interested in research on spark ignition, it is important to know that the sparking voltage of a given gap may differ greatly from the nominal when the voltage is applied impulsively by an induction coil, and moreover that the rate of rise of the impulse varies with the current in the primary winding of the induction coil connected to the gap. This latter fact may be usefully employed when it is required to get a variation of sparking voltage without altering the gap width. But when the investigation depends on the use of a capacity spark and it is deemed necessary or convenient to use an induction coil as the source of energy, it is usually preferable to place a diode valve between the induction coil and the condenser connected to the gap, and arrange for the condenser to be charged slowly through the valve, thus enabling a virtually steady voltage to be applied to the gap.

A gap having a low impulse ratio is sometimes termed a fast gap, and, by comparison, one having a high impulse ratio is termed a slow gap. If a fast and a slow gap are connected in parallel and adjusted so that both have the same nominal sparking voltage, an impulsive voltage applied simultaneously to both gaps will cause sparking only at the fast gap. A curious consequence of this is sometimes met with in practice, when it is found that a spark fails to take the path intended for it and prefers a longer and unintended alternative path.

From the above comments it will be easy to understand that the sparking voltage of a plug is not determined solely by the width of its gap. Two plugs of different design, but having the same gap width, may differ both as regards their nominal sparking voltage and their impulse ratios, and the difference in the latter quantity may be much greater than in the former. It might be expected, therefore, that the incendivity of the spark given by one of the plugs would differ very considerably from that of the spark given by the other, bearing in mind that ignition depends on the capacity component, and the energy discharged in this component varies as the square of the sparking voltage.

Another fact connected with sparking plugs is that the impulsive sparking voltage depends on whether the central insulated electrode is connected to the positive or the negative terminal of the magneto or ignition coil, the sparking voltage being usually lower when the central electrode is negative than when positive.

Recognition of the above facts ascertained by measurements of sparking voltages on plugs not mounted in an engine but in, say, a pressure chamber, has led plug designers to incorporate artificial ionizing devices in the plugs with the object of reducing the impulsive sparking voltages to a value more closely approaching the nominal sparking voltage. But as such devices have not come into general use it is reasonable to infer that they have not been accompanied by any marked benefits when the plugs are operating in engines. Some tests made by E. A. Watson[35] possibly provide an explanation. He found that the voltage measurements obtained in engine tests were substantially lower than those obtained in laboratory tests, and he attributed this condition to heating of the central electrode, the effect of the heating being to lower the density of the layer of gas in immediate contact with that electrode and so to facilitate the passage of the sparks.

CHAPTER VII

IGNITION THEORIES: THE THERMAL THEORY

THOSE of the preceding chapters which deal with ignition are concerned solely with facts ascertained from experiments and, in the recording of the facts, interpretation in terms of any theory of ignition has been studiously avoided. The reader's attention will now be directed to the principal attempts which have been made to co-ordinate the facts, or interpret them in terms of some fundamental action.

It will have been noticed that all localized sources of ignition (sparks, flames, and hot solids) have similar characteristics. Their incendivity depends upon temperature, size, and time. A source of given size and at a given temperature (provided the latter is sufficient) requires to remain in contact with the gas to be ignited for a certain interval of time. Increase of the temperature of the source is accompanied by a reduction of that time. Keeping the temperature and time fixed, the incendivity of the source is increased by increasing its size. Moreover, with a source of given size, increase of temperature not only reduces the time involved, but also the energy required to effect ignition.

The Thermal Theory

Seeing that igniting agents of all the three kinds examined (sparks, flames, and hot solids) have similar igniting characteristics, it is reasonable to assume that their ability to cause ignition is due to a common cause, and the obvious common cause is heat. It is natural, therefore, to start with the assumption that ignition is due to the heat imparted by the source to the inflammable gas mixture by which it is surrounded. But this assumption is of little or no use by itself. It must be put into a form which is closely related to experimentally ascertained facts, and is capable of useful development.

It has been mentioned (p.30) that when a spark insufficient to

cause ignition is passed in a gas it is seen to be surrounded by a small aureole of flame. By sufficiently increasing the energy dissipated in the spark and consequently the size of the aureole, ignition will ensue. This fact is the basis of the hypothesis put forward by R. V. Wheeler[36] that ignition depends on the heating of a sufficient volume of the gas to a sufficient temperature. The implications of this hypothesis were developed and embodied in a paper by E. Taylor-Jones, R. V. Wheeler, and the writer, entitled "The Form of the Temperature Wave spreading by Conduction from Point and Spherical Sources."[37]

The conception on which the development of the Wheeler hypothesis is based is very simple, but a brief explanation may serve as a useful introduction to the mathematical description to be given later. Let it be supposed that an experimenter is confronted with the task of ascertaining how much heat is required to raise to its boiling temperature a quantity of water in a metal vessel, by means of an electrical immersion heater consisting of a wire coil of known resistance placed in the water, and that the quantity of heat required to effect the desired result is to be ascertained by measuring the electrical energy supplied to the heater. Further, let it be supposed that the rate of heat generation can be varied by means of an adjustable resistance. Also let it be supposed that while heat is being imparted to the water by the heater, it is also being lost by the water to the surrounding air through the wall of the vessel. It is at once apparent that the amount of heat energy required to be imparted will depend on the rate at which it is imparted. If the rate is too slow an indefinitely large quantity of heat could be transmitted through the water without bringing it to the desired temperature. The quantity will be least when it is imparted at the highest possible rate, for in that condition the loss to the atmosphere through the vessel will be least. Of course, if the vessel were adequately enclosed by a thermally non-conductive jacket, the amount of heat energy required to raise the water to the boiling point would be independent of the rate at which the heat was imparted, as there would then be no loss to the atmosphere, and the quantity of heat energy required would be a constant quantity.

When heat is being imparted by a spark, flame, or hot solid to a surrounding gas, the portion in the immediate neighbourhood of the source of heat is both receiving heat from the source and losing it to the more remote portions, and the quantity accumulated in the proximate portion in a given time will depend on the rate at which the heat is imparted.

With the help of the above simple, though perhaps crude, illustration, it should no longer be a matter of either surprise or mystery that the incendivities of sparks and other hot local ignition sources should possess the (at first) perplexing differences disclosed by experiments, and it will also be apparent that these differences are such as might be consistent with those which are implicit in the supposition that ignition can be regarded as a thermal action.

In the words of the above-mentioned paper[37]: "The starting point in an examination of the manner in which thermal energy is conveyed to a gaseous mixture by an electric spark is given by an inquiry into the manner in which the distribution of temperature varies with time when a source of heat corresponding in general character with a spark is introduced into a gas. Electric sparks can be divided into two main classes: (1) those of exceedingly short duration (such as single capacity sparks), and (2) those of relatively long duration (such as inductance sparks). It will be advantageous, therefore, to consider the thermal distribution in a gas afforded by hypothetical sources of heat of (1) instantaneous, and (2) continued character. In order also to obtain some idea of the effect of the volume of an electric spark on its igniting power, or incendivity, point and spherical sources of heat will be considered.

The problem is here treated mainly as a problem in thermal conduction in a uniform medium, and, to avoid complication, the medium chosen is air. The numerical results obtained may not represent at all closely the manner in which heat actually spreads from a spark in an inflammable mixture. In a full treatment of the problem, the effect of the pressure wave emanating from the spark, and the effects of convection, radiation, conduction through the electrodes, and variable conductivity of the medium must be taken into account. Above

all, the fact that during the process of ignition chemical combination is proceeding causes the temperature wave to be more elevated than it would be as a result of a purely physical transmission of heat. The general effect of the heat added to the system by chemical action would be to intensify those differences that are shown to arise from purely physical causes between one type of source of heat and another.

The immediate purpose being to inquire what influence, if any, the manner of supply of heat to the medium has upon the wave form, it will be supposed that the total quantity of heat (Q) supplied is constant. This quantity will be assumed to be supplied to the medium either at a point or throughout a space symmetrically surrounding a point which is taken as the origin. Under these circumstances the temperature θ at any point in the medium at a distance r from the origin and at any time t after heating begins can be deduced from the well-known equation—

$$kr \frac{d^2\theta}{dr^2} + 2k \frac{d\theta}{dr} = r \frac{d\theta}{dt} \tag{1}$$

which expresses the fact that the excess of heat flowing into any elementary concentric shell through the inner surface, over the heat flowing out to regions beyond, is equal to the heat stored during the same time in the element. The coefficient k is the thermometric conductivity of the medium—that is to say, its thermal conduction divided by its thermal capacity c per unit volume.

The supply of a constant quantity of heat Q under four different conditions will be considered—

(1) Instantaneously at the origin.
(2) At the origin at uniform rate during time T.
(3) Instantaneously over a spherical surface of radius a.
(4) Instantaneously throughout a spherical volume of radius a.

The following numerical values, appropriate to air as the medium, will be assumed throughout: $k = 0{\cdot}5$, $c = 0{\cdot}00014$, both in c.g.s. units. The total heat Q will be taken as 0·001 calorie, and the original temperature of the medium will be assumed to be 0° C.

(1) Instantaneous Point Source

The solution of equation (1) for this case was given by Fourier in the form—

$$\theta = \frac{Q\varepsilon^{-r^2/4kt}}{8c(\pi kt)^{3/2}} . \quad . \quad . \quad . \quad (2)$$

Values of θ, the temperature in degrees centigrade for various values of r and t calculated from (2) are given in Table 1.

TABLE 1

t sec.	Temperature at					
	0	0·05	0·075	0·1	0·15	0·2 cm.
0	∞	0	0	0	0	0
0·001	14,350	4,111	862	97	0·2	0
0·002	5,074	2,716	1,244	416	20	0·2
0·003	2,762	1,820	1,081	521	65	3·5
0·004	1,794	1,313	888	514	108	12
0·005	1,283	999	731	472	135	23
0·006	976	793	611	424	150	35

At any distance r from the origin the temperature of the air reaches the highest value it can attain there after an interval of time, $t = r^2/6k$. Thus at a distance of 0·05 cm. the maximum temperature is reached after 0·00083 sec., and at a distance of 0·1 cm. it is reached after 0·00333 sec.; at this latter distance the temperature of the air never rises higher than 526.°

If an inflammable mixture of the same thermal properties is assumed to be substituted for the air, and the ignition temperature of this mixture is assumed to be 700°, then the greatest volume of the mixture that can be simultaneously raised (by conduction of heat only) to a temperature not less than this ignition temperature is approximately that of a sphere 0·091 cm. in radius, or about 3·16 cu. mm. This volume may be regarded as a measure of the incendivity of the instantaneous point source of heat (with respect only to its ability to disseminate heat by conduction) for comparison with the other hypothetical sources shortly to be discussed.

The time at which the temperature of the gas at a distance 0·091 cm. from the origin reaches its maximum (namely 700°)

is about 0·00275 sec. The form of the temperature wave at this time is shown by curve A, Fig. 32, in which the abscissae are values of r, and the ordinates temperatures.

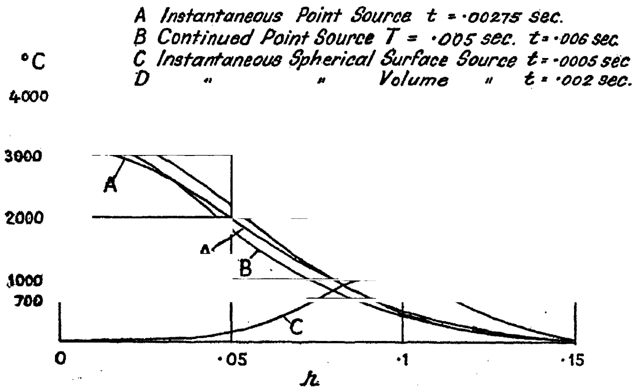

FIG. 32

The distribution of temperature due to different quantities of heat supplied instantaneously at the origin is easily calculated from Table 1, the temperature at any place and time being proportioned to Q.

(2) Continued Point Source

The solution of equation (1) for the case in which heat is supplied at the origin at a uniform rate q per sec. for a time interval T is obtained by integration from equation (2). When the time t for which the temperature is calculated is less than T the solution is—

$$= q \int_0^t \frac{\varepsilon^{-r^2/4kt}}{8c(\pi kt)^{3/2}}\, dt$$

which with the substitution $z = r/2\sqrt{kt}$ becomes

$$\theta = \frac{q}{2kc\pi^{3/2}r} \int_{\frac{r}{2\sqrt{kt}}}^{\infty} \varepsilon^{-z^2}\, dz \tag{3}$$

When t is greater than T, the solution takes the form–

$$\theta = \frac{q}{8c\pi^{3/2}} \int_0^T \frac{\varepsilon^{-\frac{r^2}{4k(t-T)}}}{[k(t-T)]^{3/2}} dT$$

$$\frac{q}{2kc\pi^{3/2}r} \int_{2\sqrt{kt}}^{2\sqrt{k(t-T)}} \varepsilon^{-z^2} dz \qquad (4)$$

In Table 2 are given numerical values of θ calculated from equations (3) and (4) for a total quantity of heat of 0·001 calorie supplied uniformly during 0·005 sec., that is to say—

$$q = \frac{Q}{T} = \frac{1}{5} \text{ cal./sec.}$$

TABLE 2

t sec.	Temperature at				
	0	0·05	0·075	0·1	0·15 cm.
0·001	∞	518	54	3	0
0·002	∞	1,197	283	58	1
0·003	∞	1,641	517	154	9
0·004	∞	1,952	714	258	26
0·005	∞	2,181	876	358	51
0·006	3,391	1,841	956	444	80
0·007	1,890	1,303	838	470	109

It will be seen from Table 2 that after the heat supply ceases the temperature at points near the origin (for example, at a distance $r = 0{\cdot}075$ cm.) rises a little before falling, in consequence of the diffusion of the heat throughout the medium. Again, assuming an inflammable mixture with an ignition temperature of 700° to be substituted for the air, this temperature is approximately the maximum temperature attained at a distance $r = 0{\cdot}0855$ cm., and is reached after the interval of time $t = 0{\cdot}006$ sec. The temperature wave at this time is shown by curve B, Fig. 32. Thus the greatest volume which is raised to at least 700° (by conduction alone) is that of a sphere of radius 0·0855 cm. or 2·62 cu. mm. This volume accordingly represents the incendivity of the continued point source of heat. The incendivity of a point source of total heat

0·001 calorie uniformly in action over 0·005 sec. is thus 17 per cent less than that of an instantaneous point source of the same total heat.

Similar calculations for the values of the time of heat supply T showed that as T is increased the surface representing the 700° limit continues to shrink, and that as T is diminished the temperature distribution continually approaches that given by an instantaneous point source ($T = 0$) of the same total heat. The incendivity of a source of small rate of heat supply may therefore be very much less than that of an instantaneous source of the same total heat.

The general conclusions to be drawn from a comparison of Tables 1 and 2 are (*a*) if an inflammable mixture is to be ignited by a given quantity of heat supplied at the point, the more quickly it is supplied the better; and (*b*) the total quantity of heat supplied by a given source is no criterion as to its incendivity unless the rate of supply is also specified.

(3) Instantaneous Spherical Surface Source

The distribution of temperature when the heat is supplied instantaneously and uniformly over a spherical surface has been stated by Lord Kelvin. In this instance if a is the radius of the spherical surface the temperature at any point distance r from the surface is given by—

$$\theta = Q \frac{\varepsilon^{\frac{-(r-a)^2}{4kt}} - \varepsilon^{\frac{-(r+a)^2}{4kt}}}{8car\pi^{3/2}(kt)^{1/2}} \qquad (5)$$

Some values of θ calculated from equation (5) with a taken as 0·1 cm. and q as 0·001 calorie are given in Table 3.

As might be expected, the temperature in the neighbourhood of the source falls to small values much more rapidly with the spherical surface source of heat than with the instantaneous point source (Table 1). Thus with the spherical surface source the temperature after an interval of time $t = 0{\cdot}002$ sec. is at no point in the medium as high as 700°. It can be shown that at time $t = 0{\cdot}0005$ sec. the volume of the spherical shell bounded by the surfaces $r = 0{\cdot}075$ cm. and $r = 0{\cdot}115$ cm. is at or above 700° (see curve C, Fig. 32). This volume is 4·605

TABLE 3

t sec.	r cm.				
	0	0·05	0·1	0·125	0·15
0	0	0	∞	0	0
0·0005	1·8	166	1015	435	55
0·001	97	411	718	420	137
0·002	416	540	507	347	181
0·003	522	527	414	299	182
0·004	514	412	356	265	175

cu. mm., which is considerably greater than the greatest volume raised simultaneously to or above 700° by the instantaneous point source, and is 1·76 times as great as the maximum obtained with the continued point source (Table 2). Arguing solely on the distribution of heat by conduction it is therefore to be expected that the effectiveness of a source of ignition will be improved by spreading it over a surface rather than by concentrating it into a small space. It is also a fair conclusion that a number of simultaneous sparks arranged close together in parallel would be more effective than a single spark of the same length and the same total heat content.

(4) Instantaneous Spherical Volume Source

For this case the solution is obtained by integration of equation (5). Thus if q is the heat generated instantaneously per unit volume of a spherical source of radius a, so that

$$Q = \frac{4}{3}\pi a^3 q,$$

$$\theta = \frac{q}{2cr(\pi kt)^{1/2}}\int_0^a x\,dx\left\{\varepsilon^{\frac{-(r-x)^2}{4kt}} - \varepsilon^{\frac{-(r+x)^2}{4kt}}\right.$$

$$= \frac{3Q}{4ca^3\pi^{3/2}}\left\{\int_0^{\frac{r+a}{2\sqrt{kt}}}\varepsilon^{-y^2}\,dy \cdot \int^{2\sqrt{kt}}\varepsilon^{-y^2}\,dy\right.$$

$$\frac{3Q}{4ca^3\pi^{3/2}} \cdot (kt)^{1/2}\left\{\varepsilon^{\frac{-(r-a)^2}{4kt}} - \varepsilon^{\frac{-(r+a)^2}{4kt}}\right. \qquad (6)$$

The temperatures given in Table 4 are calculated from equation (6) with $a = 0 \cdot 05$ cm. and $Q = 0 \cdot 001$ calorie. The initial temperature of the source is 13,640° C.

TABLE 4

t sec.	r cm.				
	0	0·05	0·1	0·125	0·15
0	13,640	13,640	0	0	0
0·001	7,207	3,388	284	38	2·5
0·002	3,530	2,174	498	160	40
0·003	2,162	1,518	526	236	88
0·004	1,493	1,130	494	264	124
0·005	1,105	879	447	268	143

Comparison of this table with Table 1 shows that at the times given in the tables, the temperature at short distances from the centre, due to the spherical volume source, is lower, and at greater distances is higher, than that due to the instantaneous point source. The greatest volume raised to or above 700° by the spherical volume source is nearly the same as that raised by the instantaneous point source—namely the volume of 0·091 cm. in radius. With the spherical volume source this is effected after a time $t = 0 \cdot 002$ sec. The form of the temperature wave at this time is shown by curve D, Fig. 32.

It appears, therefore, for the particular values assumed in the above calculation that there is no advantage to be gained, from the point of view of the distribution of heat by conduction, in enlarging the source of heat from a point to a uniformly supplied spherical volume 1 mm. in diameter; and that both are inferior to a spherical surface source of 2 mm. diameter. It is clear, however, that much more effective distribution of temperature can be obtained by further increasing the size of the source of heat. The best possible source of ignition is obviously such a volume of the inflammable mixture as can be raised instantaneously by the given quantity of heat Q to its ignition temperature; any further spreading out of the source, either in space or in time, can only result in a diminution of the volume that is simultaneously raised to

the ignition temperature, and no improvement can be attained by altering the shape of the volume initially heated. With $Q = 0{\cdot}001$ calorie and an assumed ignition temperature of 700° the volume of the most effective source for ignition is 10·2 cu. mm. (that is to say, the volume of a sphere of radius 0·1345 cm.) a figure which represents the maximum incendivity according to the scale of measurement defined.

The results of the above calculation show that, if a source of ignition be regarded solely as a source of heat, the effectiveness of a given quantity of heat in raising a sufficient volume of an inflammable mixture to a given temperature (by conduction alone) depends essentially upon the manner in which the heat is communicated to the mixture. Differences in the heat contents of the least sparks of different types capable of igniting a given gas mixture are therefore to be anticipated. To quote a single example, it has been found that the energy necessary to ignite a certain coal gas-air mixture by a capacity spark was 0·00025 joule, and by a comparable inductance spark 0·0006 joule. The ratio of these figures is of the order of magnitude which would be anticipated from a purely thermal theory of ignition (cf. discussion of Tables 1 and 2). It will be apparent from the foregoing that the observed differences in spark energy required for ignition of a given gas are such as are consistent with a purely thermal theory."

Subsequently, Professor E. Taylor-Jones published a paper entitled "Spark Ignition"[10] and based on a lecture to the British Association in 1928. In this paper he expressed the results of his mathematical investigation in a slightly different form which provides a useful supplement to the paper above quoted. He says, "One of the earliest experimental results published on this subject was an observation by Thornton that the heat dissipated in a spark just sufficient to cause ignition is less if the spark is produced by the discharge of a condenser than if it is produced (in low tension or inductance sparks) by separating the electrodes from contact so as to interrupt a current in an inductive circuit. An explanation of this result based on the view that spark ignition depends upon the volume of the gas which the spark can by its own heat raise to the ignition temperature was suggested by Taylor-

Jones, Morgan, and Wheeler. A condenser spark of very short length between metal points being regarded as an instantaneous point source of heat in a uniform medium, the temperature θ in its neighbourhood is represented by Fourier's expression—

$$\theta = \frac{Q\varepsilon^{-r^2/4kt}}{8c(\pi kt)^{3/2}} \quad . \quad . \quad . \quad . \quad (1)$$

in which Q is the quantity of heat dissipated in the spark, k is the thermometric conductivity and c the thermal capacity per unit volume of the gas, r is the distance from the source, and t is the time after the moment at which the heat is communicated. If an inductance spark be regarded as a source in which the heat is supplied to the gas at a uniform rate over an interval of time T, the temperature distribution may be deduced from (1) by integration. In the paper cited, the results of numerical calculations based upon (1) were given, which showed that in the case considered the volume of the spherical portion of the gas, the boundary of which was first raised to a certain temperature, was greater in the case of the instantaneous source than in that of a source in which the heat supply was continued at a uniform rate for a finite interval of time, the total heat supplied being the same in both cases.

The general proof that this result holds also for a point source in which the heat Q is supplied over a finite interval of time, whether uniformly or not, may be arrived at in the following manner: In Fig. 33, let curve A represent the form of the temperature wave (θt) at any distance r from an instantaneous point source. The temperature at this distance rises rapidly to a maximum and falls more slowly from it. The maximum temperature is attained at the time $t = r^2/6k$, and is higher the shorter the distance r from the source, being in fact inversely proportional to the cube of the distance from the source, as may be seen by substituting this value for t in (1). If we now suppose that the heat Q is communicated in two equal parts in an interval of time T (represented in Fig. 33 by 0·005 sec.), the temperature at the same distance is given by the sum of the ordinates of the two curves B and C, each of which has one-half the amplitude of A. The maximum in the resultant curve occurs at a time shortly before the maximum

of the second component, and it is evident that the resultant maximum is smaller than the sum of the maxima of the two components, and therefore than the maximum of the original curve A. The resultant maximum also evidently diminishes as the interval of time between the two components increases.

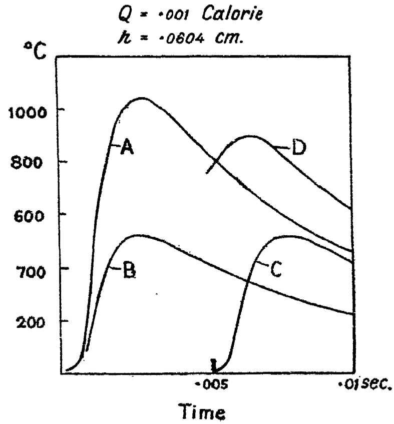

FIG. 33

We may conclude that the result of dividing the heat supplied into two equal instalments separated by any finite interval of time is to lower the maximum temperature at any given point in the neighbourhood. Similar considerations show that the same result holds if the two instalments are unequal, also if the heat is divided into three or more instalments, equal or unequal, supplied at equal or unequal intervals of time. The limiting case of a continued source, i.e. a very large number of infinitesimal instalments following one another at infinitely short intervals of time, is also included. Curve D, Fig. 33, shows a portion of the temperature wave at the same distance from a point source of the same total heat, but in which the heat supply is continued uniformly for 0·005 sec.

The general result may be stated as follows: If a given quantity of heat is supplied at a point of a uniform conducting medium in any manner during a finite interval of time, the maximum temperature at any neighbouring point is lower than

it would have been if the heat had been supplied all at the same instant.

By considering the distance from the source at which the temperature first rises to a given value, instead of the maximum temperature at a given distance, we arrive at the following corollary of the above theorem: If a given quantity of heat is supplied at a point of a uniform conducting medium in any manner during a finite interval of time, the volume of the medium, the boundary of which is just raised to any given temperature, is smaller than it would have been if the heat had been supplied all at the same instant. This follows from the theorem and the result, previously stated, that for instantaneous sources the maximum temperature diminishes with increasing distance from the source.

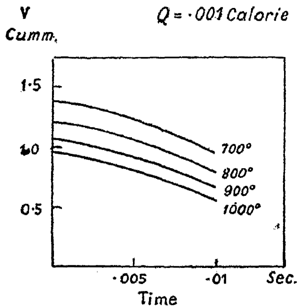

FIG. 34

The introduction of 'volume' instead of 'distance' in the corollary follows from the assumed uniformity of flow of heat in all directions. Since, however, the proof of the theorem does not depend upon the precise form of curve A in Fig. 33, the theorem and its corollary are applicable to the case of a point source in a conducting medium between two plane parallel non-conducting walls at a short distance apart, or to that of a point source in a thin column of conducting material bounded laterally by non-conductors. If in these cases the bounding walls are made conducting, some of the heat would enter the walls and would thus be lost to the medium between them, but since there seems to be no reason for supposing that the medium would lose more heat in this way with the instantaneous source than with the divided or continuous source, we may assume the theorem and its corollary to hold also in this case.

The magnitude of the effect of the duration of the heat supply is illustrated by the curves in Fig. 34, in which the ordinate represents the volume of gas, the boundary of which is just raised to a definite temperature by a point source of

heat continued at a uniform rate for a time T represented by the abscissae. The volumes are calculated from the integral of the expression (1) for four temperatures (within the range of the ignition temperatures of methane-air mixtures) and values assumed for the constants are—

$$Q = 0{\cdot}001 \text{ calorie} \qquad k = 0{\cdot}2188$$
$$r = 0{\cdot}0604 \text{ cm.} \qquad c = 0{\cdot}00032$$

It will be seen that the volume is greatest for an instantaneous source ($T = 0$) and that it diminishes steadily as the duration of the heat supply is increased. The same holds when the heat supply, instead of being continued uniformly for time T, is divided into a given number of equal instalments supplied at equal intervals over this time. It is the increase in the total duration of the heat supply rather than an increase in the number of instalments which causes the reduction in the volume raised to the given temperature. An increase in the number of instalments (supposed equal and equally spaced in time) without increase in the total duration has the opposite effect.

According to the hypothesis that ignition depends upon the volume of the gas which is raised to the ignition temperature, it follows from the corollary stated above that an instantaneous point source of heat is more effective in ignition than a point source in which the heat is supplied in any manner (continuous or discontinuous) over a finite interval of time."

Coward and Meiter[38] approached the problem from another angle. Using a methane-air mixture they first ascertained by experiment the volume of the mixture consumed by a spark just not sufficient to cause ignition, and in this way they were able to form a close estimate of the least volume of the mixture which had to be ignited to produce a self-propagating flame. With a spark in a gap of 1 mm. and a mixture containing 8·47 methane, the volume consumed by a capacity spark was about 0·90 cu. mm. The writer had found that the energy required to produce the least igniting capacity spark in an 8·8 per cent methane-air mixture in a 1-mm. gap was 0·0009 calorie. Making use of this figure, Coward and Meiter calculated with the aid of Fourier's equation the volume of the mixture

that could be heated by the spark to the ignition temperature. They found that the volume that could be sufficiently heated to cause ignition was somewhere between the limits of 0·87 and 1·24 cu. mm. They say: "The calculations depend on a number of assumptions. . . . While, therefore, a close comparison of the results with the calculated volumes of heated gases is not justified, it may be reasonably concluded that there is satisfactory agreement between the order of the results and those calculated from thermal data, and that this is evidence which supports the so-called thermal theory of ignition of gases by the electric discharge. . . . Nothing in the results of the present experiments suggests the intervention of any electric effect of the spark as the 'fons et origo' of ignition, other than the thermal effect of the degradation of its electrical energy."

One of the deductions from the thermal theory is that the energy required to effect ignition diminishes as the rate of dissipation of energy is increased. It is not easy to arrange an experiment in which the rate of dissipation of the energy of a spark can be controlled and ascertained. But in this connection the experiment described in Chapter IV, in which a solid explosive material was ignited by a very small electrically heated wire, is relevant. Attention has already been directed to the fact established by this experiment that the amount of heat energy required to effect ignition varies with the rate at which the energy is expended. The figures given in the table on page 58, when plotted, give a straight line relationship between energy and time. Calculations made by Professor E. Taylor-Jones, based on the assumptions made in the paper already described, also show that the relation between energy and time should (in the case of a point source) be linear over the same range of values of time as that in the table on page 58, though at very small values of time the energy varies slightly less rapidly than according to the linear relationship which holds at larger values. The evidential value of these results can be disputed only if it can be proved that the incendivity of a spark depends upon an entirely different property from that of a hot wire or a flame, and this, so far as the writer is aware, has not yet been established.

It will now be apparent that the thermal theory does

co-ordinate in a satisfactory manner the main results of experiments made on different types of localized igniting agents (sparks, flames, and hot solids) and that it emerges naturally out of a basis of observed facts. That the igniting agent must be capable of heating sufficiently a sufficient volume is a fact which can be demonstrated. That heat was the immediately observable characteristic of the three different sources examined is obvious. What the above-described thermal theory does is to correlate these facts. That it does so with success is apparent. But it does no more. It does not explain, and it has never been claimed that it explains, the process or so-called mechanism of ignition, that is to say, the manner in which the igniting agent, by its interaction with the surrounding gas, effects ignition. Also it does not cover the exceptional case of the ignition of hydrogen and chlorine by the action of light. It does, however, adequately and usefully cover the facts with which it deals, but before a final opinion can be made on the validity of the theory, the alternative theories must be examined.

Before describing the alternative theories, it may be useful to interpose a short comment on the conceptions underlying the terms Activation and Ignition Temperature, and this will be done in the next chapter.

CHAPTER VIII

A COMMENT ON ACTIVATION AND IGNITION TEMPERATURES

C. N. HINSHELWOOD[39] says that reactions in the gaseous state nearly always involve re-arrangement of non-polar linkages. Such linkages are formed by the sharing of a pair of electrons by two atoms. Since the non-polar linkage involves the fusion of two atoms into one structure, it appears probable that a re-arrangement of non-polar linkages will usually take place only if a certain amount of energy is first communicated to the molecule. This communication of energy is called activation, and is one of the most important factors in determining chemical transformation. "If now (still quoting Hinshelwood) the interaction of a molecule AB with an atom C is considered, it may happen that the combination AC is more strongly linked than AB. If A, B and C were put together, AC would be formed. But if AB is first formed and then C allowed to approach, the fact that A and B in AB are already in a position of minimum potential energy may render the re-arrangement to give AC and B impossible without the previous separation of A and B to some extent. This is called activation, and obviously demands the addition to the molecule AB of a certain number of quanta of vibrational energy. Vibrational quanta are the significant ones in the process of chemical activation." Later, in describing the activation process, he says: "Two molecules must be in collision at the moment of transformation, so that the activating process might be the collision itself. We thus have two possibilities, (*a*) a collision between two molecules of sufficient violence to provide the energy, (*b*) a collision of any kind between two molecules endowed with the right amount of vibrational energy." After examining these possibilities, Hinshelwood concludes that "The general coherence of results would seem to justify the statement that an activating collision is not merely a necessary but a sufficient condition for chemical transformation."

With the help of Hinshelwood's comments it becomes easy

to see the significance of heat in a chemical reaction. The thermal motions of the molecules must be sufficiently energetic to cause activating collisions.

Attention will now be directed to the distribution of velocities among the molecules of a gas. At a given temperature and at a given instant the molecules are not moving relatively to each other with the same speed. The greater number are moving at speeds approximating to the mean speed, but some few are moving at considerably lower speeds and others at considerably higher speeds. The manner in which the velocities are distributed was ascertained by Maxwell and two curves representing the Maxwellian distribution in hydrogen are shown in Fig. 35.[40] Curve *A* corresponds to a temperature of 0° and curve *B* to a temperature of 1000° C. The peculiarity of these curves is that the *area* of each represents the same number of molecules. The abscissae represent velocity, and the ordinates are quantities derived from the Maxwell equation. For the present purpose interest centres solely in the fact that the abscissae represent velocities, and the area the number of molecules in the volume of gas to be heated to different temperatures. It will be noticed that each curve has a maximum value. This occurs at what is termed the "most probable velocity." The mean velocity is slightly greater, and the mean square velocity differs only slightly from the mean velocity. At a given temperature the number of molecules moving at a speed greater than 2·5 times the mean velocity is very small and can for the present purpose be neglected. It will be noticed that on curve *B* has been drawn in dotted lines a triangle which corresponds fairly closely to the curve. Its right-hand side terminates at a point equal to 2·5 times the mean velocity represented by the apex of the triangle. As it is much easier and quicker to draw triangles than to evaluate the complex function represented by the curves, this procedure has been adopted in Fig. 36. The validity of the argument which follows is in no way affected by this approximate treatment. In Fig. 36 are drawn a number of triangles derived from the two curves shown in Fig. 35, and representing the velocity distribution at 0°, 100°, 400°, 500°, 600°, and 1000° C., the first and last corresponding to *A* and *B*

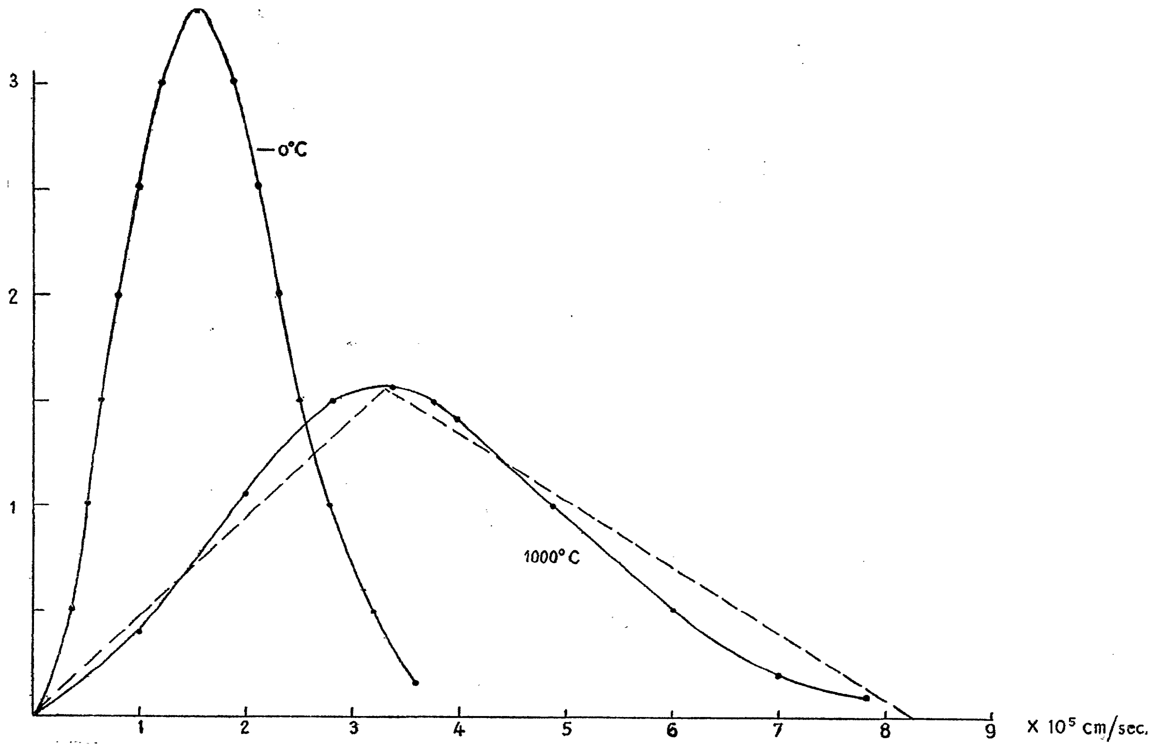

FIG. 35

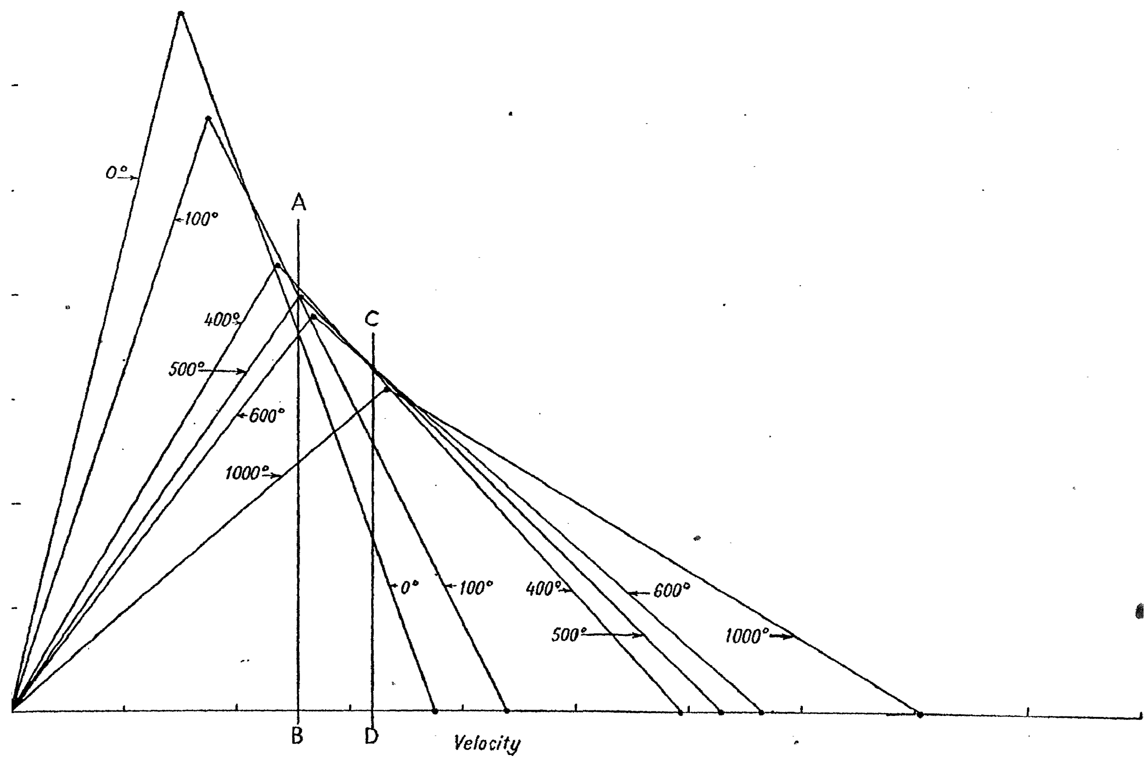

FIG. 36

in Fig. 35. It will be noticed that the curves and triangles are not quite symmetrical, the area to the right of the maximum being rather larger than that to the left.

Let it be supposed that the triangles relate to a combustible gas mixture the ignition temperature of which is 500° C., and for the purpose of the present argument comparison will first be made with the triangle marked 400°. At this latter temperature ignition would not occur; only on raising the temperature to 500° would ignition begin. A remarkable fact disclosed by these two triangles is that both include a very arge proportion of molecules moving at the same speeds. To bring out this point a line *AB* has been drawn through the apex of the 500° triangle, and attention will first be confined to the condition at the right-hand side of that line. Between that line and another line *CD* drawn through the intersection of the triangles, the 400° triangle contains slightly more molecules moving at the velocities corresponding to the lines *AB*, *CD* than the 500° triangle. It is only after passing to the right of *CD* that the 500° triangle begins to embrace faster-moving molecules than the 400° triangle, and it is apparent from comparison of the two triangles that the area bounded by the two right-hand sides beyond the point of intersection *CD* is very small in relation to the total area of either triangle. From this it is to be inferred that the significant effect of heating the gas from 400° (which is a long way below the ignition temperature) to 500°, at which ignition will begin, is to cause a relatively small number of molecules to move at faster speeds than those which exist in the gas at 400° C.

At 500°, which is assumed to be the lowest temperature at which ignition can be obtained, the ignition lag would be relatively long. The lag would be considerably reduced if the gas were heated to 600°. The effect of increasing the temperature is shown by the corresponding triangle. The increase in the number of fast-moving molecules resulting from the increase of temperature from 500°–600° is not quite so large as when the temperature was increased from 400°–500°, but the increase is of practical importance, because it is known that such an increase of temperature results in a large reduction of ignition lag.

Hinshelwood[39] has elucidated the same point by means of a calculation. He has shown that whereas in a gas heated to 1000° K. the proportion of molecules having kinetic energies of translation in excess of a certain amount is only 0·0045 per cent, on increasing the temperature to 2000° K. the proportion is increased to 0·67 per cent; that is to say, doubling the (absolute) temperature increases the energies in excess of a certain amount by more than one hundred times.

From the foregoing it becomes apparent that ignition depends not on the molecules moving at or about the mean speed appropriate to a given temperature, but on a relatively small number of molecules moving at much higher speeds than the mean. There must, however, be present a sufficient number of these high-speed molecules if ignition is to occur. Looking again at the 400° triangle it will be seen that it does embrace high-speed molecules, but not as many as the 500° C. It may be concluded, therefore, that ignition depends on the presence of a sufficient concentration of molecules moving at speeds capable of causing activation, and "ignition temperature" may be defined as the temperature at which the gas to be ignited contains a sufficient concentration of molecules capable of causing activation. From this point of view "ignition lag" at once becomes intelligible. Moreover, from this point of view the mechanism of ignition also begins to become intelligible, assuming always that ignition depends upon thermal activation.

CHAPTER IX

IGNITION THEORIES (*continued*)

(*a*) RADIATION, (*b*) IONIZATION, AND (*c*) CHAIN THEORY

A SOURCE of ignition, whether it be a spark, a flame, or a hot solid substance, has associated with it not only heat, but also radiation and ionization, and it has often been suggested that the incendivity of such a source, and particularly of an electric spark, may be attributable to one or the other of these two latter effects.

Radiation

With the exception of the familiar hydrogen-chlorine reaction on exposure to light, there is no evidence that any of the combustible gas mixtures which are usually studied in connection with this subject (that is to say, fuel or mine gases) have been ignited by the sole action of radiation of any kind. Professor Thornton(8) has mentioned that his colleague, Mr. J. R. Thompson, found it possible to ignite a cold explosive mixture by the incidence of X-rays on a platinum surface. The nature of the gas was not specified, and the presence of the platinum surface in the experiment makes it possible to suggest that the resulting ignition may have been due to action at the surface of the platinum. On general grounds it is difficult to believe in the possibility of radiation being a potent source of ignition, for the reason that most gases absorb but little energy from streams of radiation passing through them. However, this does not justify rejection of the suggestion that radiation may be capable of causing ignition. The chief reason for rejection is the failure of well-directed efforts to find supporting evidence. If radiation had any considerable degree of potency it would have been detected by these efforts. That radiation, and particularly the radiation from an electric spark, may have some effect cannot be altogether denied. But if it has any effect it is very small. An instance has been mentioned in Chapter IV. Hinshelwood(39) says that there is nothing

impossible in principle about the radiation theory, but at least one objection to the theory is that except at very high temperatures the amount of radiation present per unit volume of a gas at normal presure is very small compared with the kinetic and internal energy of the gas molecules, and this makes it probable that activation will occur by collision rather than by absorption of radiation.

Ionization

Few if any workers on this subject have failed to be attracted by the interesting prospect involved in the suggestion that ignition may be due to ionization. It may be that the opening up of this vista was due to Sir J. J. Thomson, who suggested at a British Association Meeting in 1910 that electrically charged particles might be effective in promoting chemical action in a gas. Interest in the possibility that ignition may be attributable to ionization rather than to heat was probably stimulated in the first instance more by the well-known pioneer work of Professor W. M. Thornton than by that of any other investigator.

Most investigators have probably taken as their starting point the well-known fact that hot wires begin to give off ions at about the temperature at which they are capable of starting inflammation of a combustible gas mixture, and from this fact the generalization has been made that ignition by sparks and flames as well as hot wires may be due in some way to the ions and not to the heat associated with them. But as soon as appropriate tests are applied, difficulties begin to be evident, and it quickly becomes apparent that if ions *qua* ions play any part in starting a reaction it is extremely difficult to discover. Indeed, the investigator may soon find himself prepared to endorse (perhaps with disappointment) the statement by Lind[41] that "it is not known whether gas ions discharged at an electrode produce any chemical effect."

Hinshelwood[39] summarizes the position well in the following cautious and judicious terms: "Since the nature of chemical combination is electrical, it is natural to inquire whether there is any essential connection between chemical activation processes and ionization. From the early days of the electron

theory experiments have been made with the object of establishing such a relationship, but most of the evidence seems to indicate that any ionization accompanying ordinary chemical reactions is very small and probably of a purely secondary character. Theoretical consideration, moreover, of the physical nature of the activation process, and its limit, the resolution of the molecule into atoms, suggests that there is no direct connection between ionization and stimulation of the vibrational degree of freedom of the molecule. . . . For all these reasons it seems preferable to regard the ionization phenomena as secondary. Although the opposite view has not infrequently been stated, and must be given every consideration, it appears at all events to be clear that electrical phenomena of a measurable kind actually manifest themselves in gaseous reactions to an insignificant extent."

Whilst it is difficult to prove that the free ions associated with a hot igniting source promote chemical reaction in a gas, it is not difficult to prove that such reaction can proceed without the ions. J. J. Thomson, by introducing a gold-leaf electroscope directly into a mixture of hydrogen and chlorine and causing them to react under the stimulation of light, showed that no free charges are produced either in the "induction" period or during vigorous reaction. Moreover, X-rays projected into the same system caused the gold leaf to discharge but failed to increase the rate of combination of hydrogen and chlorine.

The following experiment is also relevant.(42) A short helix of platinum wire was mounted in a chamber containing a very weak mixture of coal gas and air, and was heated by an electric current. (A thin platinum wire becomes incandescent when exposed to a sufficiently rich coal gas-air mixture. This effect does not occur with a very weak mixture.) The heating of the wire was such that it approached but did not reach the glowing temperature. There was also arranged close to the wire an insulated metal piece connected to a charged electroscope situated outside the chamber. At the temperature of the wire in this part of the experiment there was no discharge of ions from the wire and consequently no discharge of the electroscope, whether the latter was charged positively or negatively.

There was, however, a reaction (without inflammation) between the constituents of the gas mixture, this being proved by the fall of pressure in the chamber shown by a gauge connected to the chamber. While combination was taking place there was no discharge of the electroscope. The character of the experiment was then changed. The current was increased until the wire showed a dull red glow. In this condition *positive* ions were emitted by the wire. The electroscope was consequently given a positive charge to avoid discharge by the emission from the wire. The gas reaction now proceeded much more vigorously than before, but still without inflammation. Also the electroscope remained unaffected, showing that the reaction was not accompanied by any observable ionization other than the positive ionization given off by the wire. Finally a richer mixture was used, so that the wire which was now only slightly heated by the current glowed in the presence of the gas. So long as there was no inflammation there was no discharge of the positively charged electroscope. But when the interaction of the gas mixture proceeded so rapidly as to produce flame, the electroscope was discharged instantly. The experiments were repeated with iron and copper wires, and also with a mixture of ether vapour and air, and the same results were obtained. The experiments showed that ionization did not appear until flame appeared, and that the ionization was a consequence of and not a cause of inflammation. In the conditions of these experiments the observed reaction was attributable solely to the heat generated in the wire.

The writer shares the general belief that when ignition of a combustible gas mixture is effected by a hot source, the ions associated with the source play no part, as such, in causing or assisting the reaction in the mixture. Nevertheless, it must be admitted that there exists in the minds of some a condition ranging from uneasy suspicion to unqualified denial of that belief, and as this condition cannot be ignored all significant evidence must be carefully examined.

The proposition that ignition by an electric spark is an effect due directly to ionization, implies that ignition by an electric spark is an effect which is essentially different from ignition by a flame or hot solid. The facts recorded in the preceding

chapters show that the incendivities of all sources of these three kinds have the same general characteristics, and it is a reasonable inference that all three depend upon the quality which they have in common, namely, heat. The inference is strengthened by the evidence that ions, *per se*, appear to take no part in the ignition process. But there is a further piece of evidence which ought to be introduced at this point. It has already been made clear that when a spark insufficient to cause inflammation is passed through a combustible gas mixture, a small portion of the mixture is consumed. By passing a considerable number of sparks through the mixture the quantity of the mixture consumed can be measured. In one experiment[43] a weak coal gas mixture (initially at atmospheric pressure) was used, and through this was discharged a stream of small high-tension sparks produced by an induction coil having a trembler interrupter in its primary circuit. Variation of the energy dissipated in the sparks was effected by varying the current in the primary circuit of the induction coil, and to minimize the complicating effect due to the capacity component being more active than the inductance component, a high resistance was included in the secondary circuit. This reduced the capacity component to a minimum, and the main characteristic of each spark was therefore that of its inductance component. In the first place the heating effects of the spark streams in the small combustion chamber containing the spark gap was measured by the change of pressure in the chamber consequent upon change of current in the primary winding of the induction coil. Then the amount of gas consumed by the different spark streams was measured. It was found that the amount of combustion was exactly proportional to the heating effects of the spark streams. In a somewhat similar experiment by Coward and Meiter they found that the amount of gas consumed was nearly proportional to the square of the current in the primary circuit of the spark-producing coil. As the spark energy is dependent on the square of the primary current, it can be inferred that the results obtained in these two experiments are in substantial agreement. They fall into line with the others which have been recorded in earlier chapters, and they only add to the already large

accumulation of evidence that supports the conclusion that an electric spark causes ignition by its heat.

It is sometimes said that the ionization to which spark ignition is attributable is a factor which is measurable in terms of the current flowing in the spark. But the evidence is against this. One piece of evidence is that the quantity of gas consumed when an electric spark passes through it is found to be proportional to the energy of the spark and not the current, excepting in the possible case of a corona discharge at low gas pressure where the voltage remains constant over a wide range of current variation, and even here it is the product of amperes and volts that is significant. Another piece of evidence is to be found in the above-described experiment by Taylor-Jones (p. 23), in which he found that a capacity spark failed to cause ignition where an inductance spark succeeded. He estimated that the maximum current in the condenser spark was not less than 25 amps., whereas the maximum current in the inductance spark did not exceed a few hundred milliamps.

Again, it is sometimes said that whilst it may be agreed that a flame or hot solid effects ignition by thermal action, this is not so as regards an electric spark, and that this latter depends wholly or mainly on the action of its ions. This statement at once creates a dilemma. It has been shown that sparks, flames, and hot solids all have similar igniting characteristics. Also Coward and Meiter have shown that the amount of heat associated with the least igniting spark is just about the amount required to heat to a sufficient temperature a sufficient volume of the gas necessary for ignition. If the spark did not operate through its heat, but through some other property, then its heat must have been inert, and the untenable conclusion is reached that a given quantity of heat which is admittedly able to cause ignition when it is associated with a flame or hot solid is incapable of achieving that result when associated with an electric spark.

However, the conclusion that ignition by sparks or other hot local sources is attributable to thermal action is not universally accepted, and it now becomes necessary to examine certain important work by Professor G. I. Finch and his collaborators,

who may be regarded as leaders among recent advocates of the electrical theory of ignition.

In an investigation by Finch and Thompson[44] of the spark ignition of a carbonic oxide-air mixture, they used in the spark gap circuit a condenser and a variable inductance. The condenser was charged from a transformer through a diode valve to a voltage of 8300, and the spark was formed by discharging the condenser through the inductance, which was in series with the gap. The gap electrodes consisted of aluminium rods of 5 mm. diameter and having hemispherical ends. The incendivity of the spark was ascertained by varying the gas pressure in the explosion chamber containing the gap (the lower the pressure at which ignition could be effected the greater being the incendivity of the spark). They used several condensers of different capacities and carried out a series of experiments with each. It is not necessary for a proper appreciation of their experiments to quote all their results, those given in the following table being sufficient. The inductance of the coil used in the spark circuit is expressed by the number of turns L in the coil.

Capacity of Condenser	$\frac{1}{2}CV^2$ joules	L Coil Turns	Least Igniting Gas Pressure (cm.)
0·041	1·43	6 8 14	75·8 74·9 70·0
0·051	1·76	6 8 14	74·6 73·8 64·4
0·066	2·30	6 8 14	73·8 69·3 56·5
0·071	2·45	6 8 14	73·1 66·6 50·0

The results show that, keeping the capacity constant, increase of inductance had the effect of increasing the incendivity of the spark. The conclusions drawn by the authors from the above results are as follows: "It has now been shown that

under the conditions in question the igniting power of a spark due to the discharge of a condenser through an inductive circuit is determined by the natural frequency of the circuit to such an extent that a suitable decrease in frequency may completely outweigh the effect of any possible reduction in igniting power due to either a decreased amount or rate of energy dissipation, or both, by either the first half oscillation of a spark or by the entire discharge. According to the thermal theory, however, 'ignition depends on the heating of a sufficient volume of the gas by conduction to a sufficient temperature,' which also implies that 'the heat energy required in the source to produce ignition is least when the heat is imparted instantaneously. When the rate of heat supply is less a greater quantity of heat must be given to the gas before ignition can occur.' Hence it is clear that the conflict between the thermal theory and the facts set forth herein is complete. Therefore the mechanism of electric spark ignition and *indeed of ignition as a whole* cannot be adequately explained in terms of any purely thermal theory. On the other hand, the electrical hypothesis is consistent with and capable of explaining *all known facts* relating to the ignition of gases. For, according to this view, ignition being primarily determined by the setting up of a sufficient concentration of suitably activated constituent molecules, the imparting of energy to the molecules in such a manner as to bring about either an insufficient or excessive degree of activation is wasteful from the point of view of causing ignition. Now it is well known that the greater the frequency of a condensed discharge the higher is the level to which the molecules are thereby activated. Thus the high-frequency spark is in general a rich source of ionization, whereas the low-frequency arc spectrum reveals mainly the presence of neutral atoms or molecules. Further, we have shown previously that the cathodic combustion of carbonic oxide detonating gas is determined by a prior activation which falls short of complete ionization of the carbonic oxide.

"In view of the foregoing facts and considerations, we conclude that ignition is determined by the setting up of a sufficient concentration of suitably activated molecules and that in our experiments a reduction of frequency resulted in an increase

in the ratio between energy usefully expended in the production of suitably activated molecules and that otherwise dissipated."

By activation, Finch and Thompson mean "any increase in the internal energy of a molecule; quantized when the molecule as such remains intact, but generally unquantized when ionization or atomization occurs."

It will be noticed that their conclusion contains two statements, (*a*) that ignition is determined by the setting up of a sufficient concentration of suitably activated molecules, and (*b*) that a reduction of frequency resulted in an increase in the ratio between the energy usefully expended in the production of suitably activated molecules and that otherwise dissipated. Statement (*a*) would be accepted by supporters of the thermal theory, as it is consistent with that theory, and is in line with the statements of Hinshelwood quoted in Chapter VIII, and the consideration of the thermal motions of molecules described in that chapter. Statement (*b*) is the interpretation by Finch and Thompson of the fact ascertained by their experiment that increase of inductance in the path of a condenser discharge across a spark gap had the effect of increasing the incendivity of the spark. These conclusions have been developed in mathematical form by G. Mole.[45]

Reverting again to the experiment by Taylor-Jones described on page 23, he found that when sparks were formed between the hemispherical ends of electrodes of 8 mm. diameter by means of a discharge in an inductive circuit containing a variable condenser (the inductance remaining constant), the incendivity of the spark was increased by decreasing the capacity of the condenser. When he first encountered this result he thought it was contrary to the thermal theory. But on examining the spark, he noticed that the diminution of capacity was accompanied by wandering or spreading of the spark in the gap, and he attributed the increased incendivity to this fact. Moreover, Taylor-Jones has found that if the frequency of a condenser-gap circuit is lowered by the inclusion of an inductance coil, the sparks show evidence of a tendency to wander.[2]

The statement of the thermal theory in the terms quoted by Finch and Thompson—"the heat energy required in the

source to produce ignition is least when the heat is imparted instantaneously"—is correct only so long as the spark size remains unchanged, as was explained in Chapter VII. It was shown in that chapter that the incendivity of a spherical-surface source is greater than that of a point source. The conclusion reached by Taylor-Jones was that the result obtained in his experiment was consistent with the thermal theory, on account of the spreading out or enlargment of the volume of the spark which occurred when the capacity was reduced. The experiments by Taylor-Jones and by Finch and Thompson appear to be essentially similar, but whereas the former regarded his results as consistent with the thermal theory, the latter have formed the opposite conclusion.

It might be asked whether a comparison could be made between the Finch and Thompson experiments and those made by the writer (see page 21), in which it was found that increase of the capacity of the condenser was accompanied by increase of incendivity. On looking again at the Finch and Thompson results (page 116), it might be said that they also found that with a given number of inductance turns in the spark circuit increase of the condenser capacity resulted in increased spark incendivity. But it must be pointed out that in the Finch and Thompson experiment increase of capacity was accompanied by increase of the energy provided for spark production, whereas in the writer's experiment, that energy was kept constant. The two experiments are therefore not identical.

The Finch and Thompson experiments appear to bring out no new essential fact, and therefore provide no evidence for resolving the conflict between the rival thermal and electrical theories. What they do is to afford further evidence of the previously known fact that a change in the character of an electric discharge is accompanied by a change of incendivity. They provide no ground for the assertions that "the mechanism of spark ignition and indeed of ignition as a whole cannot be adequately explained in terms of any purely thermal theory, and that the electrical hypothesis is consistent with and capable of explaining all known facts relating to the ignition of gases."

An earlier paper by Finch and Cowan[46] is of considerable

importance, as the results which it describes may be so interpreted as to make it possible to find a basis for an electrical theory and to link this up with the thermal theory. In the work described in this paper, Finch and Cowan used electric

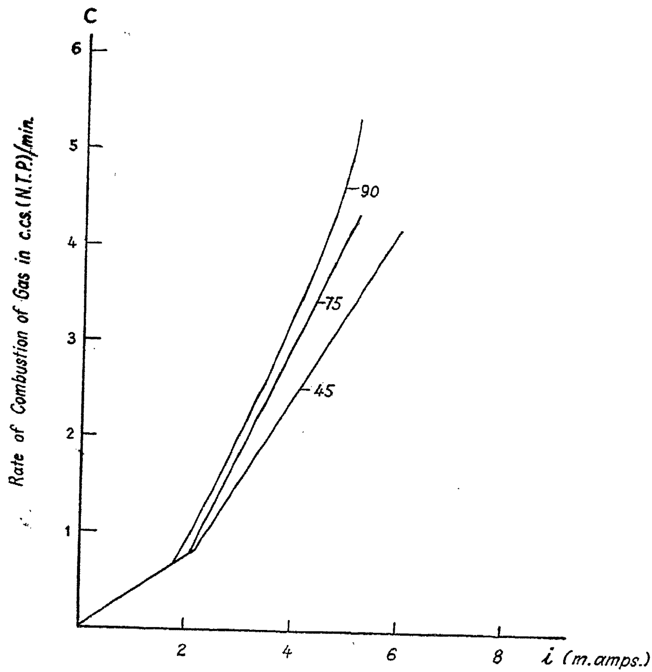

FIG. 37

glow discharges in electrolytic gas at very low pressures (45–90 mm. of mercury). The discharges were caused to form over gaps of different widths (varying from 1·8–15 mm.). In one set of experiments the gap electrodes were made of copper and in another of platinum.

From the tables of results given in the paper the writer has selected those obtained with copper electrodes set at 3·8 mm. apart, and these have been put into the form of the graph as shown in Fig. 37, in which the current (i) passing the discharge

in milliamps. is plotted against the rate of combustion (c) of electrolytic gas in c.c. at normal temperature and pressure per min. The gas pressures in the different experiments were 45, 75, and 90 mm. of mercury respectively.

Two remarkable results are evident in the graph. At low current values in the discharge the rate of gas consumption was proportional to the current and independent of the pressure. With a gas pressure of 45 mm. the initial straight line suddenly takes a different direction from about the point $i = 2{\cdot}2$. The same happens at about the point $i = 2$ when the pressure is 75 mm. and at about the point $i = 1{\cdot}7$ when the pressure is 90 mm. It is evident from the graph that whilst the rate of combustion was independent of the pressure at low current values it ceased to be so at higher current values, and the point of departure from the one condition to the other moves nearer to the origin with increase of pressure. The more important of the deductions made by Finch and Cowan from these results are that—

(1) An electric discharge can be passed through electrolytic gas in such a manner that combination takes place at a rate which is determined only by the current passed by the discharge.

(2) Up to a certain limiting current which depends upon the nature of the cathode, the gas pressure, and the degree of separation of the electrodes, combustion is confined to the cathode zone.

(3) Such cathodic combustion is independent of the potential fall between and the degree of separation of the electrodes, the gas pressure, and the temperature of the discharge, but depends on the nature of the cathode material.

(4) The rate of such cathodic combustion is directly proportional to the current.

(5) After a certain limiting current has been exceeded, combustion commences abruptly in the inter-electrode zone and is thereafter superposed upon the cathodic combustion, the two then continuing as independent simultaneous effects.

(6) The said inter-electrodic combustion is itself, like the cathodic, proportional to the current passing; unlike the

cathodic, however, it is independent of the material of the electrodes, but dependent upon the gas pressure and the degree of separation of the electrodes.

They then add: "From these facts it may be concluded that the combustion which occurred under the said conditions was primarily determined by the ionization of the gaseous medium through which the current passed."

As regards the rate of combustion being proportional to the current, it may be mentioned that the voltage across the electrodes was substantially constant, and therefore it could be said with equal correctness that the rate of combustion was proportional to the energy of the discharge. The Finch and Cowan conclusions have been examined by J. M. Holm[(48)] and he formed the opinion that the results of their experiments "might be explained equally well upon the thermal theory."

Later, Guenault and Wheeler[(49)] repeated the Finch and Cowan experiments and obtained substantially the same results. In addition they measured temperatures in the path of the discharge. Their results are shown in the graph at Fig. 38. Guenault and Wheeler conclude that the "combination of hydrogen and oxygen in the direct-current discharge is *not* primarily determined by its ionizing effect; the ability of the discharge to cause chemical reactions in electrolytic gas by electronic excitation of the molecules may be materially assisted by its thermal effect." It will be seen that on the basis of the same facts, Guenault and Wheeler reach an almost entirely different conclusion from Finch and Cowan. Nevertheless, there appears to be a shade of uneasiness underlying the terms in which Guenault and Wheeler have expressed their conclusion.

Subsequently the writer tried by means of further experiments to get a fuller insight into conditions that might be properly regarded as relevant to the problem presented by the Finch and Cowan results. Among these experiments was the following: Using a small induction coil having a trembler interrupter in its primary circuit, a stream of thin sparks was caused to flow across a 2-mm. gap between the ends of a thin brass rod and a needle point. The purpose of this combination of electrodes was to keep the sparking voltage as steady as

possible, prevent lateral wandering or spreading of the spark, and reduce to a practical minimum the surface exposed by the electrodes to the gas in the immediate neighbourhood of the spark stream. The gas used in the combustion chamber was a very weak coal gas-air mixture at atmospheric and higher

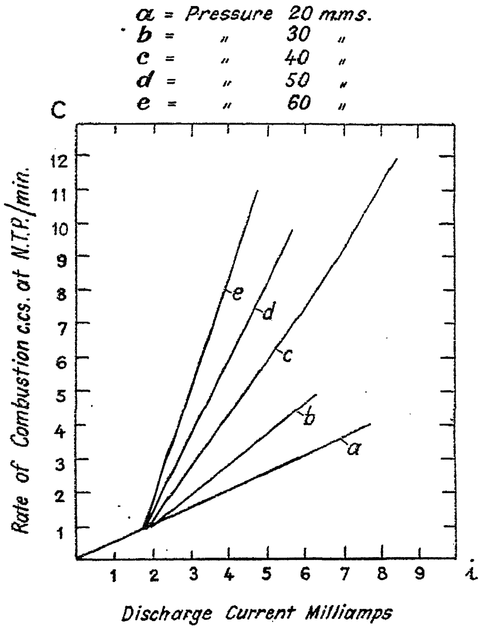

Fig. 38

pressures, and the quantity of energy discharged in the spark stream was varied by adjustment of the primary current supplied to the coil. In each experiment the discharge across the gap was maintained for one minute, and the amount of gas consumed was measured by the drop of pressure in the chamber as shown by a water gauge. The heating effect of the discharge was measured by filling the chamber with air and noting the increase of pressure shown by the water gauge. It was found that over the range required for the experiments

the heating effect was proportional to the square of the current in the primary winding of the induction coil, and the results showed that the gas consumed was exactly proportional to the heating effect of the spark stream. Also, the results showed that the amount consumed with a given rate of discharge increased with increase of gas pressure. The results are shown in Fig. 39. The relevance of these results is to be found in the fact that keeping the electric discharge rate constant, the amount of gas consumed increased with increase of gas pressure. If the rate of gas consumption had been dependent solely on the current in the spark stream, the results should have been independent of the pressure. On the hypothesis that the rate

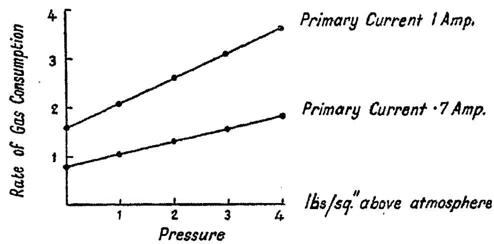

FIG. 39

of gas consumption was dependent on the thermal action of the spark stream, the fact that the rate of gas consumption depended also on the pressure was only in accordance with expectations. These results are consistent with those shown in the upper portions of the graphs shown in Figs. 37 and 38. In the writer's opinion his results can be explained only in terms of the heating effect of the spark stream, and it is submitted that the same explanation can equally well be applied to the upper parts of the Finch and Cowan results, an opinion which apparently was also formed by Holm and by Guenault and Wheeler in connection with their work. The interest and probable importance of the Finch and Cowan results is to be found in the lower portion of the graph at Fig. 37, when the rate of gas consumption was independent of the pressure, a fact which was confirmed by Guenault and Wheeler.

In a later paper by Finch and Cowan(47) they described a

study by them of the ignition of electrolytic gas by means of similar discharges to those described in their earlier paper, and stated that the "conclusions are drawn that ignition is conditioned by the attainment in some portion of the gas traversed by the discharge of a certain definite concentration of suitable ions or electrically charged particles in the building up of which water vapour materially assists, and that flame propagation is also essentially an electrical phenomenon."

Bearing in mind the quotation from Hinshelwood that "an activating collision is not merely a necessary but a sufficient condition for chemical activation," and the fact that ionized molecules can be given a high rate of speed in an electric field, it seems possible on the basis of the results shown in the lower portions of Figs. 37 and 38 that when the gas pressure is sufficiently low and the mean-free-paths of the molecules are in consequence sufficiently large, and moreover so long as the rate of energy discharge is not too high, activation is due wholly or mainly to ionized molecules moving at a high speed under the action of the electric field. But with increase of gas pressure the activation depends increasingly on thermal action, until at sufficiently high pressures activation results wholly from thermal action.

It will now be apparent why the writer attaches importance to the Finch and Cowan experiment. It contains, in his opinion, definite evidence of electrical as distinct from thermal activation, in the conditions mentioned, though they do not warrant the conclusion that electrical activation results from the action of a spark in a gas at pressures approaching or exceeding atmospheric pressure. It must be recognized that high speeds can be given to molecules by both thermal and electrical actions, and it would appear from the Finch and Cowan experiments that at low gas pressures the speeds attained by electrical action may possibly be sufficient to effect activation by collision.

Summarizing the above comments on the thermal and ionization theories of ignition, the thermal theory as described in Chapter VII does not attempt to give an explanation of the mechanism of ignition. What it does is to harmonize in a simple hypothesis a large array of apparently discordant and

previously irreconcilable facts. To change the metaphor, it "tidied up the mess" that existed at the time when it was formulated, and provided not only a useful starting point for further investigation but also a valuable general guide to practical problems connected with the ignition of gases by sparks and other hot sources—a purpose which it still usefully serves. But the need for exploring more closely the mechanism of ignition remained, and in this field the work of Professor Finch and his collaborators has played a conspicuous part. Their disapproval of the thermal hypothesis is unquestionable, but to what extent their experimental results can be said to support their conclusions is a matter that can best be left to individual judgment.

The Chain Theory

In more recent years an approach to the problem has been started by others on other lines, these being guided by the ideas underlying the chain theories of chemical reactions. G. Gimmdmann and N. Neumann[50] from an investigation of the electric spark concluded that ignition is a purely thermal process which could be explained by a chain mechanism in which the role of the spark is to create a number of active centres whose concentration is approximately equal to the spark energy.

The subject in terms of the chain theory is treated mathematically in a paper by H. G. Landau[51] entitled "The Ignition of Gases by Local Sources." He says: "In order to treat the problem mathematically it is necessary to adopt a definite physical mechanism for the process. We conceive of the problem of the ignition of gases as follows: In a combustible gaseous mixture contained in a large vessel there is an arrangement for rapidly releasing energy within a small volume at a distance from the walls; for example, by passing an electric spark. It is assumed that the energy instantaneously heats up a small spherical volume and also creates active particles. These active particles are the chain carriers of the chain-reaction theory: it is not necessary to state whether they are ions, atoms, molecules with an excess of energy, or something else. It is also not necessary to specify the mechanism by which

these active particles are created, but simply to assume that the release of energy does create them. The following processes then take place: There is a heat-generating reaction which is assumed to proceed at a rate proportional to the concentration of active particles, but this concentration varies with distance and time because the active particles are diffusing through the gas and in addition are increasing in number at a rate proportional to their concentration; that is, chain-branching is occurring. We are interested mainly in temperature and so the chemical reaction enters the picture only in so far as it generates heat; it is not necessary to make any statements about the mechanism of the reaction except that it proceeds at a rate proportional to the concentration of active particles. Similarly no particular mechanism for chain-branching need be introduced. Now the temperature at the centre of the sphere tends to fall because of conduction of heat away from it and to rise because of the heat generated. Some criterion for ignition is needed and the most natural one to use is the requirement that the temperature at the centre of the sphere shall never fall. This can be justified by the fact that both the rate of the heat generating reaction and of the chain branching increase with increasing temperature, so that a temperature drop would slow them down, thus causing a further drop of temperature and eventually making the reaction stop altogether. In the following section the partial differential equations for the concentration of active particles and for temperature are stated and solved. Then the criterion for ignition is applied, giving a relation between the physical constants which must hold for ignition. To make clear exactly what is involved we re-state in more general terms the problem which is treated here. Consider a heat-conducting medium of infinite extent which is initially at temperature T_0 except within a sphere of radius R, where the initial temperature is T_1. At the start this sphere is filled with active particles in the concentration of n_0 per unit volume. These active particles diffuse through the medium. Each generates Q units of heat in unit time and they increase in number at a rate proportional to their concentration. We wish to determine the relation that must exist among the physical constants for the temperature

at the centre of the sphere never to decrease. The differential equation for the concentration of active particles is—

$$\frac{dn}{dt} = \mu^2\nabla^2 n + an \quad . \quad . \quad . \quad (1)$$

with the initial condition

$$\left.\begin{array}{l} n = n_0 \text{ for } 0 \leqslant r < R \\ n = 0 \text{ for } r > R \end{array}\right\} \text{when } t = 0 \qquad (2)$$

where $n = n$ (r.t.) is the concentration of active particles at a distance r at time t

μ^2 = diffusion coefficient
∇^2 = Laplacian differential operator, here

$$\nabla = \frac{1}{r^2} \cdot \frac{d}{dr}\left(r^2 \frac{d}{dr}\right.$$

a = branching coefficient
n_0 = initial concentration in the sphere of radius R."

Landau then proceeds with the mathematical development of his argument, and concludes with the following comments: "Unfortunately the result obtained cannot be tested by direct comparison with experiment because the quantities which enter have not been measured in experiments on the ignition of gases. In fact, they may not be capable of direct experimental determination. However, certain conclusions can be drawn from this theoretical result as it stands, and it should be possible to perform experiments which will give some information about the needed quantities. . . . Our conclusion would be that ignition of a hydrogen-oxygen mixture by a local source can occur only if the source raises some volume to a high enough temperature for branching to be significant. This statement sounds very similar to those made by the proponents of a thermal theory of ignition. However, it is obvious that our theory does not state that ignition is assured by merely raising some volume to a sufficiently high temperature." In summarizing the contents of his paper, Landau says: "When energy is released by a local source such as an electric spark in a combustible gas mixture, it is assumed to heat instantaneously a small volume and also to create active

particles, chain carriers, which diffuse through the gas and increase in number by chain branching processes at a rate proportional to their concentration. The heat-producing reaction proceeds at a rate proportional to concentration of active particles."

In the writer's opinion it is open to question whether the chain theory of chemical reaction has any relevance to the problem of ignition by local sources. The chain theory necessarily presupposes the presence of active particles called chain carriers. Before the igniting source is brought into action these particles are either non-existent or are inert. Some agency is required to bring them into existence or render them active, and the problem of ignition, in the writer's submission, is concerned solely with the process whereby the physical condition of some of the molecules of an inflammable gas mixture is so changed as to enable chemical action to occur.

Conclusion

The contents of this chapter and Chapter VII seem to show that there is more of agreement than disagreement between the advocates of the different theories of ignition. The role of the igniting source is to effect activation of some kind. The evidence is that ions as such play no part. According to Hinshelwood, activating collision is not merely a necessary but a sufficient condition for chemical transformation. The ultimate question as between the thermal and the electrical theories is whether such collisions are due to the thermal motion of molecules (whether ionized or not) or equivalent motions produced by the action of an electric field on ionized molecules. The evidence appears to show that under all normal conditions activation is by thermal collisions, but (on the basis of the Finch and Cowan experiments) activation may be caused by electronic collisions at very low gas pressures and with weak electric discharges.

In this connection, however, the above-mentioned work of Lewis and Kreutz[18] (page 41) may be significant. In that work it was shown that passing one of the constituents of a methane-air mixture through an electric spark discharge immediately before admixture with the other constituent or

constituents had the effect of lowering substantially the ignition temperature of the mixture. In discussing this fact, Lewis and Kreutz say that "the passage of the spark through the gas introduces some active carrier which when carried into the methane stream renders the latter more easily ignitable. Two properties of the carriers are conspicuous. They possess a relatively long life and are rather easily removed from the gas by metal screens." And after considering several possible explanations they say that "there remain as the most probable cause of the phenomena the electrically charged gases or ions created by the spark. The ions are carried into the methane stream, where they exert an action which facilitates combustion. What the mechanism of the action is can only be conjectured with the data available. . . . These experiments throw light on the process of ignition of a combustible gas mixture by the direct action of a spark passing through the mixture. They suggest that the ions formed in the path of the spark have a distinct auxiliary effect of their own, materially aiding the thermal energy liberated by the spark to bring about ignition of the mass of the gas."

In the above comment by Lewis and Kreutz is to be found a definite attempt to bridge the gulf which separates the protagonists of the thermal and electrical theories, and their experiment is impressive. An obvious question is, however, whether similar results would have been obtained if instead of a spark, a flame or incandescent solid had been used, this being (like the spark) insufficient to affect materially the mean temperature of the gas flowing over it, but sufficient to cause either ionization, dissociation, or increase of the internal energy of some of the gas molecules.

In conclusion, the reader will already have gathered that the fundamental difficulty associated with the ionization theory of spark ignition is that it is based mainly on an alluring supposition and that no definite supporting evidence has yet been found. Until it can be shown that ions *qua* ions are able to cause ignition of a combustible gas mixture this theory can only be regarded as a fanciful suggestion.

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